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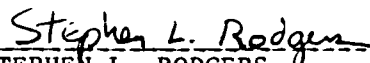
FOREWORD

This final report was submitted by United Technologies Research Center, East Hartford CT on completion of contract F04611-86-C-0071 with the Astronautics Laboratory (AFSC), Edwards Air Force Base, CA. AL Project Manager was Lt Pete Dolan.

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19. Abstract (Continued)

consideration was given to ground state molecular structures, of low molecular weight, which exhibit a high positive heat of formation. Calculations to date have been carried out on: 1) light element C_{3v} and C_{2v} structures (H_4 , Li_3H , LiH_3 , Li_4); 2) azide-like structures (FN_3 , $\alpha-N_2O_2$, $FNCO$, CO_3 , HN_3 , $FNBF$); 3) cyclic boron structures (B_3H_3 , B_2H_2NH); and 4) hypervalent structures (NF_5 , PF_5).

We find that the ground states of H_4 (tetrahydrogen), LiH_3 and Li_4 , as C_{3v} structures, are unstable toward dissociation into diatomic fragments. These molecules do not look promising as storable, high energy chemical species. We have studied the Li_3H system in both C_{3v} (trigonal pyramid) and C_{2v} (planar kite-like) symmetries. Although both structures are vibrationally stable, with the C_{2v} symmetry slightly lower in energy at the MP2/6-311G** level of theory, an analysis of the bond character in the C_{3v} and C_{2v} structures indicate that only the latter is thermodynamically stable. Using either O_2 or F_2 as an oxidizer, Li_3H appears to give about 10% improvement in I_{sp} over LiH . The optimum I_{sp} for the $Li_3H/H_2/O_2$ system is 456 seconds, which can be compared with 441 seconds for the $LiH/H_2/O_2$ system and 441 seconds for the H_2/O_2 system run at $P_c = 800$ psia, $A/A^* = 20:1$.

All of the azide-like structures are vibrationally stable with high (400–500 kJ/mol) positive heats of formation. The best candidate appears to be asymmetric dinitrogen dioxide, $\alpha-N_2O_2$, which exhibits a heat of formation of +500 kJ/mol and can deliver 450 seconds I_{sp} as a hybrid propellant with hydrogen, and advanced performance in solid propellant formulations as a replacement for AP. The energetics and pathways for decomposition of FN_3 have also been studied. Our calculations, carried out to compliment the experimental studies of FN_3 at Rockwell Science Center, indicate that $NF[a^1\Delta]$ should be efficiently produced by the thermal decomposition of FN_3 . This shows promise as a method to produce a short wavelength chemical laser. The structure of this molecule, its predicted vibrational spectrum and the role of low-lying triplet states have been examined.

None of the cyclic boron structures examined to date, which include B_3H_3 and B_2H_2NH , are highly energetic. Their chemistry is further complicated by condensation reactions which cause conversion to higher molecular weight structures.

The hypervalent NF_5 molecule has been studied as a D_{3h} structure, as the ionic $NF_4^+F^-$ form and as an inverted C_{3v} structure. Detailed calculations indicate stability for NF_5 only as a D_{3h} structure. Correlated energy calculations were carried out for NF_5 and for several azide structures. Our analysis indicates that NF_5 is a thermodynamically stable compound with a predicted heat of formation ΔH_f^0 (0 K) = + 25.1 kJ/mol. An $H_2/F_2/NF_5$ propellant system is predicted to have an optimum I_{sp} of 466 seconds ($P_c = 800$ psia, $A/A^* = 20:1$), yielding no significant improvement over the H_2/F_2 system. However, if the physical properties of NF_5 indicate the possibility of non-cryogenic storage, NF_5 may be a promising candidate for an earth storable oxidizer.

SUMMARY

A theoretical research investigation of light element species that may have potential for use as advanced propellants or as energy sources in a chemical propulsion system has been undertaken. Included in this research program were detailed quantum mechanical studies of the electronic structure of such species, an analysis of their chemical (and thermodynamic) stability and suggestions of possible synthesis routes for their formation and subsequent stabilization. The molecular species that were examined in detail were chosen from those screened to have a predicted theoretical maximum specific impulse in excess of that available from conventional chemical systems. It was also intended that this theoretical research effort should be carried out with sufficient flexibility to aid in the analysis and guidance of concurrent experimental programs of synthesis of high energy molecular species. To this end, one task of this research program, theoretical studies of the thermochemistry and dissociation reactions of fluorine azide, was carried out in parallel with an experimental research study of azide chemistry that was conducted at the Rockwell Science Center. In addition, a study of the potential of fluorine azide as a source of $\text{NF}[\text{a}^1\Delta]$ for a chemically pumped laser, was carried out for AFWL in conjunction with a parallel experimental program at Rockwell Science Center. Finally, a joint theoretical study of Li_3H as a potential fuel was carried out in collaboration with the University of Alabama.

Theoretical electronic structure calculations were carried out for several high energy species that appear to be attractive candidates for advanced chemical propulsion systems. Using deliverable specific impulse and storability as the major criteria for the evaluation of new oxidizers or fuels, primary consideration was given to ground state molecular structures, of low molecular weight, which exhibit a high positive heat of formation. Calculations to date have been carried out on: 1) light element C_{3v} and C_{2v} structures (H_4 , Li_3H , LiH_3 , Li_4); 2) azide-like structures (FN_3 , $\text{a-N}_2\text{O}_2$, FNCO , CO_3 , HN_3 , FNBF); 3) cyclic boron structures (B_3H_3 , $\text{B}_2\text{H}_2\text{NH}$); and 4) hypervalent structures (NF_5 , PF_5).

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PREFACE

This report was prepared by the United Technologies Research Center, East Hartford, Connecticut, under Contract F04611-86-C-0071. The research was funded by both the Air Force Astronautics Laboratory and the Air Force Weapons Laboratory.

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SECTION 1

INTRODUCTION

Conventional chemical systems for rocket propulsion have a predicted theoretical maximum specific impulse of approximately 389 seconds (H_2/O_2 system, 1000 psia – sea level). Although some improvements in specific impulse may be possible through development of new chemical oxidizers, no chemical system currently under development appears likely to provide a large increase above this value. On the other hand, advanced space missions presently considered need the development of propulsion systems with specific impulses of 800 to 2,000 seconds for earth orbiter travel, and much higher specific impulses for interplanetary travel. Actual operation of such systems clearly remains in the future, but exploratory studies of such systems certainly are needed at the present time. The search for high-performance rocket propellants has, therefore, of necessity turned to consideration of advanced chemical systems, including various metastable species such as He_4^* and He_2^* , compounds with large positive heats of formation (such as FN_3), and antimatter propulsion. Included among these species are stabilized free radicals, which have received considerable attention in the past. Performance considerations always make light element molecules the most promising species for advanced rocket propulsion systems and as a result, a number of efforts have been undertaken to characterize molecular structures of light element species that have a *high energy content because of the peculiar nature of their chemical bonding*. It was the goal of this research program to identify those light element molecular structures with high potential as advanced propellants and to characterize their energy content, possible synthesis routes and their chemical stability.

The advantages of using highly energetic compounds or radicals as propellants for rocket engines have been discussed by several authors (References 1-3), and the performance capabilities of such materials as the light metal hydrides or atomic hydrogen are reasonably well established. In principle, the stabilization of atomic species appears simple, and depends on keeping the atoms physically separated, thus preventing them from recombining into their thermodynamically stable molecular state. In practice, this may be achieved by dispersing the atoms in a solid matrix at temperatures low enough to prevent their diffusion through the matrix. Considering isolation of the atoms as the criteria, one could expect stabilization of up to 50% atoms for a perfect body-centered cubic arrangement. The manner of preparation by condensation from a gaseous discharge, however leads to a disordered random configuration, in which one might expect concentrations of approximately 10% (References 4 and 5). Other calculations have indicated an upper limit of about 3% (Reference 6). Atomic hydrogen as well as other atoms have been stabilized in a solid matrix at liquid helium temperatures (4 K) (References 6-9). The observed concentrations have been smaller than predicted by theory and are generally of the order of 0.2 to 0.001%.

At temperatures above 4 K, most studies have shown that diffusion sets in rapidly. Recombination then occurs and is generally complete at 20–30 K. This behavior is as expected considering the small size of the atoms and the nature of the matrices. Hydrogen atoms would therefore not be expected to have any long-term stability at temperatures near 77 K (the normal boiling point of liquid nitrogen). Similar behavior has been observed for other light element free radicals (Reference 10). In summary, efforts at stabilization by physical methods, such as matrix isolation, of significant quantities of dissociated atoms, in order to take advantage of their large energy of recombination have been quite discouraging, as evidenced by both theory and experiment.

The potentialities of another class of possible compounds in which helium is one of the constituent atoms has also been well explored. There are two types of compounds that might be formed from the noble gases such as helium. The first type is the so-called van der Waals molecule which forms when an inert atom such as helium combines with another atom or molecule. In this case the separate atoms, which are all in their ground states, form complex structures due to weak van der Waals attractive forces. It has been shown (Reference 11) that the hydrates, solvates, and mercury compounds of helium are loosely bound molecular complexes held together by forces of the weak van der Waals type. Complexes of this type have small heats of dissociation (< 2.0 kjoule/mol) and are of little use as potential energy sources.

The second type of compound that might be formed from the noble gases is the metastable structure that results when an inert atom is electronically excited by an electric arc (or other means) and combines with another atom or molecule. The possibility of forming compounds in this way arises from the supposition that, although the normal helium atom is chemically inert, helium excited to higher electronic states might behave as an alkali metal. The energy available in electronically excited states is often quite large (for example, the lowest excited state of helium, a triplet state, is approximately 1900 kjoule/mol above the ground state) and an atom excited to one of these levels and stabilized by compound formation might retain a substantial amount of this energy for subsequent release in a controlled reaction such as a chemical rocket. A most attractive molecule for such an application would be the metastable $a^3\Sigma_u^+$ state of the helium molecule since the molecular weight of the decomposition products is four and the average value of γ approaches 1.67, thus insuring efficient energy conversion in the exhaust nozzle.

Stabilization of compounds of excited helium is not likely at ordinary temperatures, but it has been suggested that low temperature stabilization might prove feasible if the average lifetime of the excited molecule is sufficient to allow trapping of the energy in a solid matrix or by other means. In order to determine the feasibility of storing an energy-rich molecule, an exact analysis of the energy levels and expected lifetimes of the excited states is required. This Research Center has carried out such a study of metastable helium compounds for the Air Force Rocket Propulsion Laboratory (Reference 12) in the early sixties. Detailed quantum mechanical studies of

several metastable helium compounds (He_2 , HeH , HeBe) were carried out to determine the energy levels and lifetimes of these species. These early calculations were at the then state-of-the-art and included some of the very first configuration - interaction (CI) studies ever carried out on excited states of diatomic molecules. After a lengthy analysis of the deexcitation mechanisms of such metastable species, it was concluded that stabilization was not likely, even in matrices at 4 K, and efforts to synthesize such compounds were phased out.

The idea of stabilizing metastable helium atoms by formation of a spin-polarized solid phase has also been proposed (References 13 and 14). This idea apparently developed from a suggestion by Garrison, et al. (Reference 15) that the lowest $^5\Sigma_g^+$ state of He_2 , formed from two metastable He atoms, exhibited weak chemical binding (0.07 eV) and no first order radiative decay process to the underlying continuum states. Arguments were given (Reference 13) that such a material should form an insulating classical solid and that the metastability could be trapped by either intrinsic effects of the condensed phase or by external influences such as pressure or electric or magnetic fields.

In an effort to analyze these proposed spin-polarized He compounds, this Center carried out a detailed quantum mechanical study of molecule formation through collisions of triplet metastable helium atoms (Reference 16). Contrary to a previous theoretical study (Reference 15), the lowest lying molecular state was found to be of $^5\Pi_g$ symmetry and all of the low-lying quintet states of He_2 were shown to arise from the ionic $\text{He}^- - \text{He}^+$ interaction. The 0_g^+ and $1g$ components mix via spin-orbit coupling to the autoionizing singlet and triplet manifolds of He_2 with a cross-section of $\sim 100 \text{ \AA}^2$. The 0_g^- , $2g$ and $3g$ components mix via spin-orbit coupling to the ionic $\text{He}^- - \text{He}^+$ manifold with radiation lifetimes of $\sim 10 \mu\text{sec}$ to the $\text{He}_2^+ + e$ underlying continuum. Thus, again we found no evidence that metastable helium compounds could be stabilized against radiative decay or autoionization processes.

The past emphasis on free radical stabilization in atomic species or metastability in helium compounds has caused many investigators to overlook the possibility of finding high-energy species, possibly suitable for propellant application, which represent molecules with steric atomic arrangements that represent localized minima on the ground state potential surface. To a certain extent, this has been due to the enormous effort required in any experimental program of screening the large number of possible molecular conformations which can be made up from, for example, the lightest four or five elements. However, theoretical techniques do exist for screening this large aggregate of possible molecules to determine those which might be sufficiently stable and energetic for propellant applications. More definitive calculations could then be made for the most promising of these species to verify the results of the screening process and to provide additional data on which to base recommendations for experimental synthesis studies.

In view of the above considerations, and because of the high performance potential of such systems, a broad, comprehensive research investigation of light-element high-energy compounds that might be useful for advanced chemical propulsion systems was undertaken by this Center for AFRPL in the late sixties (Reference 17). In particular, this study consisted of a theoretical evaluation of the possibility of high-energy propellant formation from each of the diatomic and symmetric triatomic species which could be formed from elements having atomic numbers of eighteen or less. The objective of the study was the determination of those stable or metastable chemical systems, included in the above categories, which are most likely to provide specific impulses of the order of 500 seconds or greater, and, as such, are most worthy of further theoretical and experimental investigation. Initial emphasis was mainly upon highly-excited metastable states, theoretically capable of delivering very high impulses. During the latter stages of this work, the study was broadened to concentrate more heavily on energetic ground states which might possibly be more easy to stabilize. Over 10,000 electronic states of nearly 500 molecular species were screened in that study.

In the first phase of that study emphasis was placed upon the possible use of the light, noble-gas difluorides as advanced oxidizers. In this phase, calculations were performed for the low-lying states of HeF_2 and NeF_2 and their diatomic and atomic fragments. All states of the difluorides which were investigated were found to be repulsive, as were the states of HeF and NeF . It was concluded that the light noble-gas fluorides do not constitute an attractive source of high-energy oxidizers. In the second phase of the investigation, emphasis was placed upon ascertaining the stability of a number of compounds believed to be metastable or to have a high positive heat of formation. Calculations were performed for the ground states of the polyatomics H_4Ne , H_2Ne , H_2Na , H_2Ar , O_2Ne , various possible diatomic and atomic fragments thereof, and for several low-lying states of the diatomics ONe and OAr . Except for the hydrides, such as H_2Ne , no appreciable bonding was exhibited for any molecular arrangements of the ground state of these species. It was concluded, at the time, that although several of these hydrides showed promise as high-energy species, most were ruled out for their potential use as fuels owing to their molecular weight.

Very recently, there has been a renewed interest in light element compounds in geometric arrangements other than the stable ground state form. Several authors (References 18-22) have discussed various forms for the H_4 molecule, sometimes referred to as tetrahydrogen. The systems HeH_2 and Li_mH_n have also been studied both experimentally and theoretically (References 23-30). In all of these systems, molecular arrangements have been found which correspond to an energetic local minima on the ground state potential energy surface of the reactant atoms. These high energy molecular arrangements can be referred to as strained isomeric forms. In many cases, these high energy isomeric species exhibit ionic binding, whereas the lowest energy arrangement is a covalent structure. There are many such isomeric arrangements known in

organic chemistry, the vinylidene form of acetylene, being a typical example. A survey of strained organic molecules has been given by Newton (Reference 31). Under the present research program we have carried out a systematic study of such isomeric arrangements of light element compounds, using the most advanced quantum mechanical techniques that are available, to screen those having the highest potential as advanced propellant types and to suggest possible reaction routes for their synthesis and stabilization. The results of our preliminary studies of such compounds and their performance evaluation are given below in the Discussion and Recommendations section.

The general composition of this report is as follows. In Section 2, we present a description of the mathematical methods which were employed in this research. Included in Section 2 are sub-sections which deal with the construction of electronic wavefunctions, the calculations of expectation properties, the evaluation of molecular transition probabilities, and the calculation of electronic wavefunctions using *ab initio* methods. The calculated results and pertinent discussion are presented in Section 3. Based on these present studies, we have identified several areas for further technical work. Recommendations are also presented in Section 3 and a concluding summary of this program is given in Section 4. A list of all technical presentations and publications that have resulted from this research program are given in Appendix A. Abstracts of the pertinent published papers are then collected in Appendix B. Appendix C contains a recent publication on Li_3H .

SECTION 2

MATHEMATICAL BACKGROUND

Central to these theoretical studies are the actual quantum-mechanical calculations which must be carried out for the atomic and molecular species. In particular, the methodology for computing the minimum energy reaction pathways and testing for vibrational stability must be carefully analyzed. For added clarity, various aspects of these calculations are discussed below.

Much evidence on diatomic and polyatomic systems indicates the inadequacy of minimum basis sets for constructing quantitatively correct molecular wavefunctions (References 32 and 33). This means inner-shell and valence-shell orbitals of quantum numbers appropriate to the atoms (1s, 2s, 2p, for C, N, O; etc.). The main deficiency of the minimum basis set is its inability to properly describe polarization and the change of orbital shape for systems which exhibit large charge transfer effects. Values of the screening parameters for each orbital can either be set from atomic studies or optimized in the molecule; the latter approach is indicated for studies of higher precision. When high chemical accuracy is required, as for detailed studies of the ground or a particular excited state of a system, a more extended basis must be used. Double-zeta plus polarization functions or optimized MO's are usually required as a minimum representation for reliable calculated results of chemical accuracy.

The chosen basis sets give good results only when used in a maximally flexible manner. This implies the construction of perturbation expansions or the use of CI wavefunctions with all kinds of possible orbital occupancies, so that the correlation of electrons into overall states can adjust to an optimum form at each geometrical conformation and for each state. Except when well-defined pairings exist, as for closed shell and exchange dominated systems, a single-configuration study (even of Hartree-Fock quality) will be inadequate.

Proper electronic states for systems composed of light atoms should possess definite eigenvalues of the spin operator S^2 as well as an appropriate geometrical symmetry. The geometrical symmetry can be controlled by the assignment of orbitals to each configuration, but the spin state must be obtained by a constructive or projective technique. Formulas have been developed (Reference 34) for projected construction of spin states from orthogonal orbitals, and programs implementing these formulas have been in routine use at UTRC for several years. One of the least widely appreciated aspects of the spin-projection problem is that the same set of occupied spatial orbitals can sometimes be coupled to give more than one overall state of a given spin quantum number. It is necessary to include in calculations all such spin couplings, as the optimum coupling will continuously change with changes in the molecular conformation. This is especially important in describing degenerate or near-degenerate excited electronic states.

In the sections below, we describe the several mathematical approaches that are applicable to calculation of the electronic structure of molecules, to the calculation of potential energy surfaces for chemically reacting systems, and to the subsequent calculation of radiation and collisional processes. Since several different approaches are indicated, we describe their expected areas of applicability.

2.1 Method of *Ab Initio* Calculation

2.1.1 Born–Oppenheimer Separation

For a system of n electrons and N nuclei, and considering only electrostatic interactions between the particles, we have for the total Hamiltonian

$$\mathcal{H} = \mathcal{H}_{el} - \sum \frac{\hbar^2}{2m_a} \nabla_a^2 + \frac{\hbar^2}{2M_T} \left[\sum_{\beta=1}^N \sum_{\alpha=1}^N \nabla_{\alpha} \cdot \nabla_{\beta} + 2 \sum_{\alpha=1}^N \sum_{i=1}^n \nabla_{\alpha} \cdot \nabla_i + \sum_{i=1}^n \sum_{j=1}^n \nabla_i \cdot \nabla_j \right] \quad (1)$$

where

$$\mathcal{H}_{el} = -\frac{\hbar^2}{2m_e} \sum_{i=1}^n \nabla_i^2 + V^{el}(\vec{r}_n, \vec{R}_N) \quad (2)$$

and where m_e , m_a , M_T , are the masses of the electron, atom and combined system mass, respectively. Now since the ratios m_e/m_a , and m_e/M_T are both small, ($2 \cdot 10^{-6} - 5 \cdot 10^{-4}$) we can effect a separation of the electronic and nuclear coordinates treating the total wavefunction as a product of a nuclear and an electronic part. We have

$$\psi(\vec{r}_n, \vec{R}_N) = \sum_k \chi_k(\vec{R}_N) \psi_k(\vec{r}_n, \vec{R}_N) \quad (3)$$

where $\psi_k(\vec{r}_n, \vec{R}_N)$ is an electronic wavefunction parametric in the nuclear coordinates as given in Equation (3) and $\chi_k(\vec{R}_N)$ are nuclear motion wavefunctions which satisfy (neglecting terms of the order of m_e/m_a)

$$\left[- \sum_{a=1}^N \frac{\hbar^2}{2m_a} \nabla_a^2 + \frac{\hbar^2}{2M_T} \sum_{a=1}^N \sum_{\beta=1}^N \nabla_a \cdot \nabla_\beta + V^e(\vec{r}_n, \vec{R}_N) \right] \chi_k = i\hbar \frac{\partial \chi_k}{\partial t} \quad (4)$$

The cross term in $\nabla_a \cdot \nabla_\beta$ can be eliminated by a proper change of variables and Equation (4) then reduces to a $3N-3$ dimensional Schrodinger equation.

For most systems, where the velocity of motion of the nuclei is slow relative to the electron velocity, this decoupling of electron and nuclear motion is valid and is referred to as the adiabatic approximation. Equation (3) thus defines an electronic eigenstate $\psi_k(\vec{r}_n, \vec{R}_N)$, parametric in the nuclear coordinates, and a corresponding eigenvalue $E_k(\vec{R}_N)$ which is taken to represent the potential energy curve or surface corresponding to state k .

2.1.2 Variational Methods

By an *ab initio* method is meant one that starts from a zero-order Hamiltonian which is exact except for relativistic and magnetic effects, and which involves the evaluation of electronic energies and other relevant quantities for wavefunctions which are properly antisymmetrized in the coordinates of all the electrons. For a system containing n electrons and M nuclei, the zero-order Hamiltonian depends parametrically on the nuclear positions and is of the form

$$\mathcal{H} = -\frac{1}{2} \sum_{i=1}^N \nabla_i^2 - \sum_{i=1}^n \sum_{j=1}^M \frac{Z_j}{|\vec{r}_i - \vec{R}_j|} + \sum_{1 \leq i < j}^M \frac{Z_i Z_j}{|\vec{R}_i - \vec{R}_j|} + \sum_{1 \leq i < j}^n \frac{1}{|\vec{r}_i - \vec{r}_j|} \quad (5)$$

where Z_i and \vec{R}_i are the charge and position of nucleus i , \vec{r}_j is the position of electron j , and ∇_j^2 is the Laplacian operator for electron j . All quantities are in atomic units, i.e. lengths in bohrs, energies in hartrees (1 hartree = 2 Rydbergs). The many-electron wavefunction consists of one, or a linear combination, $\psi = \sum_{\mu} c_{\mu} \psi_{\mu}$, of terms of the form

$$\Psi_{\mu}(R) = \mathcal{A} \mathcal{O}_s \prod_{i=1}^n \phi_{\mu i}(\vec{r}_i, R) \theta_{\mu M} \quad (6)$$

where each $\phi_{\mu i}$ is a spatial orbital, \mathcal{A} is the antisymmetrizing operator, \mathcal{O}_s is the spin-projection operator for spin quantum number S , and $\theta_{\mu M}$ is a product of α and β one-electron spin

functions of magnetic quantum number M_s . No requirement is imposed as to the double occupancy of the spatial orbital, so linear combinations of the form given by Equation (6) can describe a completely general wavefunction. The spatial orbitals $\phi_{\mu i}$ may be whatever basis orbitals have been introduced, arbitrary linear combinations thereof, or specific linear combinations determined pursuant to the particular calculational method in use.

The spatial orbitals $\phi_{\mu i}$, the spin functions $\theta_{\mu m}$ and the coefficients of different ψ_{μ} , if a linear combination of ψ_{μ} is used, may be explicitly determined by invoking the variational principle. Various specific methods are described below for determining wavefunctions. However, we should first observe that the adequacy of an *ab initio* calculation, or for that matter any energy calculation, will depend crucially upon the extent to which the wavefunction can be qualitatively appropriate. Some of the considerations surrounding the choice of a wavefunction are the following:

- (i) necessity that the wavefunction possess sufficient flexibility to be able to describe dissociation to the correct atomic and molecular fragments as various internuclear separations are increased;
- (ii) maintenance of equivalent quality of calculation for nuclear geometries differing in the nature or number of chemical bonds;
- (iii) ability to describe degenerate or near-degenerate electronic states when they are pertinent;
- (iv) ability to describe different electronic states to equivalent accuracy when their interrelation (e.g., crossing) is relevant, in particular, ability to describe ionic-valence state mixing;
- (v) ability to represent changes in the coupling of electron spins as bonds are broken or reformed.

The foregoing considerations indicate that it will often be necessary to consider wavefunctions with more than a minimum number of singly-occupied spatial orbitals, and that there will be many potential curves or surfaces for which a wavefunction consisting of a single ψ_{μ} cannot suffice. It will then be necessary to allow mixing of ψ_{μ} with different degrees of orbital spatial occupancy so as to obtain smooth transitions from the occupancies characteristic of separated atoms or molecules (or ions) to those characteristic of a compound system or a different fragmentation.

Another implication of the considerations surrounding the choice of a wavefunction is related to the treatment of electron spin. Not only is it necessary to require that the wavefunction

be an eigenfunction of S^2 and S_z but it is also necessary to take account of the fact that under many conditions, there will be more than one spin eigenfunction of given S and m_s . The different spin eigenfunctions correspond to different couplings among the individual spins. Since reactive processes involve the breaking and forming of electron-pair bonds, they must necessarily be accompanied by reorganizations of the spin coupling. A failure to take account of this will lead to qualitatively inappropriate wavefunctions.

In Hartree-Fock calculations $\psi(R)$ is restricted to a single ψ_μ which is assumed to consist as nearly as possible of doubly-occupied orbitals. The orbitals $\phi_{\mu i}$ are then selected to be the linear combinations of basis orbitals best satisfying the variational principle. Writing $\phi_{\mu i} = \sum_\nu a_{\nu i} \chi_\nu$, the $a_{\nu i}$ are determined by solving the matrix Hartree-Fock equation

$$\sum_\nu F_{\lambda\nu} a_{\nu i} = \epsilon_i \sum_\nu S_{\lambda\nu} a_{\nu i} \quad (\text{each } \lambda) \quad (7)$$

where ϵ_i is the orbital energy of $\phi_{\mu i}$.

The Fock operator $F_{\lambda\nu}$ has been thoroughly discussed in the literature (Reference 35) and depends upon one- and two-electron molecular integrals and upon the $a_{\nu i}$. This makes Equation (7) nonlinear and it is therefore solved iteratively. UTRC has developed programs for solving Equation (7) for both closed and open-shell systems, using basis sets consisting of either Slater-type or Gaussian-type atomic orbitals. Examples of their use are in the literature (Reference 36).

In configuration interaction calculations, the overall wavefunction has more than one term, ψ_μ , and the c_μ are determined by invoking the variational principle to obtain the secular equation

$$\sum_\nu (H_{\mu\nu} - w S_{\mu\nu}) c_\nu = 0 \quad (\text{each } \mu) \quad (8)$$

where

$$H_{\mu\nu} = \int \Psi_\mu^*(R) \mathcal{H}(R) \Psi_\nu(R) d\tau \quad S_{\mu\nu} = \int \Psi_\mu^*(R) \Psi_\nu(R) d\tau \quad (9)$$

Equation (8) is solved by matrix diagonalization using either a modified Givens method (Reference 37) or a method due to Shavitt (Reference 38) or Raffanetti (Reference 39).

The matrix elements $H_{\mu\nu}$ and $S_{\mu\nu}$ may be reduced by appropriate operator algebra to the forms

$$H_{\mu\nu} = \sum_P \epsilon_P \langle \theta_M | O_S P | \theta_M \rangle \left\langle \prod_{i=1}^n \psi_{\mu_i}(\vec{r}_i, \vec{R}_N) | \mathcal{H}(\vec{R}_N) P | \prod_{i=1}^n \psi_{\nu_i}(\vec{r}_i, \vec{R}_N) \right\rangle \quad (10)$$

$$S_{\mu\nu} = \sum_P \epsilon_P \langle \theta_M | O_S P | \theta_M \rangle \left\langle \prod_{i=1}^n \psi_{\mu_i}(\vec{r}_i, \vec{R}_N) | P | \prod_{i=1}^n \psi_{\nu_i}(\vec{r}_i, \vec{R}_N) \right\rangle \quad (11)$$

where P is a permutation and ϵ_P its parity. The sum is over all permutations. $\langle \theta_M | O_S P | \theta_M \rangle$ is a "Sanibel coefficient" and the remaining factors are spatial integrals which can be factored into one- and two-electron integrals. If the ϕ_{μ_i} are orthonormal, Equations (10) and (11) become more tractable and the $H_{\mu\nu}$ and $S_{\mu\nu}$ may be evaluated by explicit methods given in the literature (Reference 34). Computer programs have been developed for carrying out this procedure, and they have been used for problems containing up to 106 total electrons, 10 unpaired electrons, and several thousand configurations.

The CI studies described above can be carried out for any orthonormal set of ϕ_{μ_i} for which the molecular integrals can be calculated. Programs developed by UTRC make specific provision for the choice of the ϕ_{μ_i} as Slater-type atomic orbitals, as Gaussian-type orbitals, as symmetry molecular orbitals, as Hartree-Fock orbitals, or as more arbitrary combinations of atomic orbitals.

The one- and two-electron integrals needed for the above described method of calculation are evaluated for STO's by methods developed by this Center (Reference 40). For Gaussian orbitals, either the Carnegie-Mellon integral package (Reference 41) or the integral routines incorporated in the HONDO or GAMESS programs (Reference 42) can be employed.

2.1.3 Configuration Selection

Using a double-zeta plus polarization basis set of one-electron functions, a typical system can easily have of the order of 10^6 configurations in full CI (that resulting from all possible orbital occupancies). It is therefore essential to identify and use the configurations describing the significant part of the wavefunction. There are several ways to accomplish this objective. First,

one may screen atomic-orbital occupancies to eliminate configurations with excessive formal charge. Alternatively, in a molecular-orbital framework, one may eliminate configurations with excessive numbers of anti-bonding orbitals. A third possibility is to carry out an initial screening of configurations, rejecting those whose diagonal energies and interaction matrix elements do not satisfy energy significance criteria.

Another common method of classifying configurations is to examine the total number of orbitals in the wavefunction that differ from the SCF reference wavefunction. We write the CI wavefunction as

$$\psi_{CI} = C_0\psi_0 + \sum_i C_i\phi_i^S + \sum_j C_j\phi_j^D + \dots \quad (12)$$

where a single excitation function, ϕ_i^S differs from the SCF reference ψ_0 by one orbital and the double excitation function ϕ_j^D by two, and so on. The CI coefficients, C_i , are then determined variationally to yield the lowest possible total energy. In the limit of a complete basis set ($N \rightarrow \infty$), and where all possible substitutions are included in ψ_{CI} , the variational energy approaches the correct nonrelativistic Born-Oppenheimer result. Errors arise from a truncation of the functions used to determine the SCF reference wavefunction and from the truncation of the excitation functions series in ψ_{CI} . The reference wavefunction ψ_0 will typically be the same for a CI or Many Body Perturbation Theory (MBPT) calculation; however, for a molecule even as small as water, ψ_{CI} becomes a function of a very large number of basis functions. Additionally, the reference state itself may be multi-dimensional in order to describe systems such as diradicals or systems with orbital degeneracy. Because of this, one must truncate the expansion and eliminate unimportant configurations. In general one can show that

$$\langle \psi_0 | \mathcal{H} | \phi^T \rangle = \langle \psi_0 | \mathcal{H} | \phi^Q \rangle = 0 \quad (13)$$

In words, the matrix elements between the reference wavefunction and triple and quadruple excitations is zero. Thus to first order, only single and double excitations contribute. Because of this, many CI calculations attempt to include all single and double excitations in the expressions for ψ_{CI} . To go beyond this, generally more than one reference wavefunction is used. Programs to handle configurations on all the above criteria are available at UTRC.

Other, potentially more elegant methods of configuration choice involve formal approaches based on natural orbital (Reference 43) or multiconfiguration SCF (Reference 44) concepts. To implement the natural-orbital approach, an initial limited CI wavefunction is transformed to natural orbital form, and the resulting natural orbitals are used to form a new CI. The desired result is a concentration of the bulk of the CI wavefunction into a smaller number of significant terms. The multiconfiguration SCF approach is more cumbersome, but in principle more effective. It yields the optimum orbital choice for a preselected set of configurations. This approach works well when a small number of dominant configurations can be readily identified. The method is described briefly below.

2.1.4 Multiconfiguration – Self Consistent Field Method (MC-SCF)

The Hartree-Fock self consistent field method has been proven to be a powerful tool for the calculation and understanding of many ground state properties of molecules in the vicinity of their equilibrium structure. However, in most cases the one configuration Hartree-Fock approximation is not adequate to properly describe the dissociation of molecular bonds. Also, many excited states cannot be represented by a single configuration wave function. In order to calculate properties for such states, or to investigate the formation of molecular bonds, one often needs multiconfiguration wave functions for which both the linear coefficients, C_i of the configuration expansion

$$\psi = \sum_i C_i \psi_i \quad (14)$$

as well as the set of orthonormal molecular orbitals $\{\phi_j\}$, from which the configurations ψ_i are constructed, are optimized according to the variational principle. As is well known, this "MC-SCF" problem presents many more difficulties than the simple one configuration Hartree-Fock case and much work has been devoted to obtaining convergent solutions during the last decade.

The difficulties mainly arise from the fact that for general MC-SCF wave functions the energy is not invariant with respect to rotations between occupied orbitals. Hence, instead of a relatively simple pseudo-eigenvalue equation in the one determinant case, the set of coupled Fock equations

$$\sum_j F_{ij} |\phi_j\rangle = \sum_j \epsilon_{ij} |\phi_j\rangle, \quad (15)$$

with the hermiticity conditions

$$\epsilon_{ij} = \epsilon_{ji}^* \quad (16)$$

has to be solved. ϵ_{ij} are Lagrange multipliers which account for the orthonormality constraints imposed on the orbitals. The Fock operators F_{ij} depend on the orbitals $|\phi_i\rangle$ and the set of CI coefficients $\{C_i\}$. In analogy to the one determinant case many attempts have been made to solve these equations iteratively by keeping the Fock operators fixed in each iteration step. Then the Lagrange multipliers can be expressed by coupling operators constructed such that the Fock equations are transformed into pseudo-eigenvalue equations yielding the improved orbitals. These are used in a second step to determine new CI coefficients by diagonalizing the CI matrix $\langle \psi_i | \mathcal{H} | \psi_j \rangle$. The convergence of these algorithms, however, has often been found to be poor.

A second group of MC-SCF methods is based on the generalized Brillouin theorem. In these methods, the orbital changes are derived from the coefficients of a CI expansion consisting of the MC-SCF wavefunction and all one-electron singly excited configurations. A computer program (ALIS) implementing this method has been developed by Ruedenberg, et al. (Reference 45). A somewhat more elegant program (GAMESS) which also incorporates analytical gradients is also available (Reference 42). More recently, various methods have been proposed which are based on direct minimization of the energy, avoiding the Fock operators altogether. Such methods are now being studied in our laboratory and will be incorporated into our existing computer programs if they prove to be highly efficient.

2.1.5 Many-Body Perturbation Theory (MBPT)

In MBPT we again begin with the SCF wavefunction (ψ_0) as our reference and attempt to account for E_c , the correlation energy. The concept of excitation functions described in the above section on CI calculations carries over to MBPT calculations. In MBPT one can write the wavefunction, ψ_p , as

$$\psi_p = e^{\mathcal{T}} \psi_0 \quad (17)$$

where T is an excitation operator defined as

$$T = T_S + T_D + T_T + T_Q \dots \quad (18)$$

where S, D, T, and Q refer to single, double, triple, and quadruple substitutions respectively. One can write T_n , in general, where n refers to the number of excitations as

$$T_n = \frac{1}{n!} \sum_{\substack{ijk\dots \\ abc\dots}} t_{ijk\dots}^{abc\dots} \chi_a^+ \chi_b^+ \chi_c^+ \dots \chi_i \chi_j \chi_k \dots \quad (19)$$

where a,b,c,... are excited orbitals and i,j,k,... are orbitals occupied in ϕ_0 . The total energy is now given by

$$E_{\text{MBPT}} = \langle \phi_0 | \mathcal{H} e^T | \phi_0 \rangle \quad (20)$$

To evaluate E_{MBPT} , the $t_{ijk\dots}^{abc\dots}$ from above must be determined. An equivalent expression that makes the perturbation expansion clearer is

$$E_{\text{MBPT}} = \sum_{k=0}^{\infty} \langle \phi_0 | \mathcal{H} [(E_0 - \mathcal{H}_0)^{-1} \mathcal{H}]^k | \phi_0 \rangle \quad (21)$$

where the sum is over only so-called linked diagrams. \mathcal{H}_0 has eigenfunctions ϕ_0 , and the expansion is of orders in the perturbation, $V = (\mathcal{H} - \mathcal{H}_0)$. The $k = 0$ term gives the reference energy and for $k > 0$ correlation corrections are included. In practice the MBPT total energy is calculated by truncating the T operator expansion and projecting $\mathcal{H} e^{T_n} | \phi_0 \rangle$ onto the appropriate n -space. This leads to a set of nonlinear coupled equations for the $t_{ijk\dots}^{abc\dots}$ coefficients which correspond to the CI expansion coefficients. The equations are solved iteratively and E_{MBPT} evaluated. In practice T_4 is an upper limit that corresponds to quadruple substitutions. The series is an oscillatory convergent sum, which in practice has proven to be at least as accurate as E_{CI} with single and double excitations included.

The best possible method to use would be a full CI (all possible configurations) with a complete basis set. However, since the number of configurations is proportional to $(n!)^r$, where n

is the number of basis functions and ℓ is the level of excitation, it would be prohibitive to even include all single and double excitations. This truncation causes the loss of size consistency, which implies that the energy calculated for A and B as a molecular system, but dimensionally far apart, is the sum of the energy calculated for A and B separately. In a size extensive calculation the energy is proportional to the size of the system. These properties are very important if one wishes to compute correct relative energies on a potential energy surface, a necessary criteria for defining the reactive pathways of interest in this research program. MBPT, on the other hand, is guaranteed to have the correct size-dependence because the expansions contain only the so-called linked diagrams. In addition, because of the computational efficiency of MBPT, calculations can be performed up to fourth order in the perturbation expansion and include single, double, triple, and quadruple excitations in the calculation of the correlation energy. Such calculations are usually performed with at least a split valence plus polarization basis set. For the light element compounds which exhibit ionic bonding, the inclusion of diffuse basis functions and possibly higher polarization d or f-functions may be required for a more quantitative treatment.

2.2 *Ab Initio* Gaussian Wavefunction Electronic Structure Codes

Owing to the complexity of evaluating multicenter electron repulsion integrals over Slater-type (exponential) orbitals, various groups have adopted a computational approach to electronic structure calculations based on gaussian orbitals. A highly developed series of programs, named GAUSSIAN 8X ($X = 2, 6, 8$), is available from Carnegie-Mellon University (Reference 41). A second series of programs has evolved from the original version of Dupuis and King's (Reference 46) HONDO code. This code has been further developed by separate groups as GAMESS (Reference 42), CADPAC (References 47) and HONDO 7 (Reference 48). Finally a new code named COLUMBUS (Reference 49 and 50) has been developed by the Ohio State/Argonne/Battelle group. UTRC has been designated as a beta test site for this new development. A brief description of the features of these codes follows.

2.2.1 GAUSSIAN 88

GAUSSIAN 88 is a connected system of programs for performing *ab initio* molecular orbital (MO) calculations. It represents further development of the GAUSSIAN 70/76/80/82/86 systems already published. The contributors to this program include: M. J. Frisch, J. S. Binkley, H. B. Schlegel, K. Raghavachari, C. F. Melius, R. L. Martin, J. J. P. Stewart, F. W. Bobrowicz, C. M. Rohlfing, L. R. Kahn, D. J. Defrees, R. Seeger, R. A. Whiteside, D. J. Fox, E. M. Fleuder, and J. A. Pople. GAUSSIAN 8X was originally implemented on the chemistry department DEC VAX 11/780 computer at Carnegie-Mellon University. Since then this program has been installed on a number of different computers.

GAUSSIAN 88 was designed with a transparent input data stream, making this program very user friendly. All of the standard input is free-format and mnemonic. Reasonable defaults

for input data have been provided, and the output is intended to be self-explanatory. Mechanisms are available for the sophisticated user to override defaults or interface their own code to the GAUSSIAN system. In this respect, we intend to utilize GAUSSIAN 88 as a fundamental framework for several applications. Options are being incorporated into this code to provide capabilities beyond Hartree-Fock and various perturbation theory options.

The capabilities of the GAUSSIAN 88 system include:

- a) Calculation of one- and two-electron integrals over s, p, d, and f contracted gaussian functions. The basis functions can either be cartesian gaussians or pure angular momentum functions and a variety of basis sets are stored in the program and can be requested by name.
- b) Self-consistent field calculations for restricted closed-shell (RHF), unrestricted open-shell (UHF), and open-shell restricted (ROHF) Hartree-Fock wavefunctions as well as those types of multiconfigurational wavefunctions that fall within the Generalized Valence Bond-Perfect Pairing (GVB-PP) formalism.
- c) Evaluation of various one-electron properties of the Hartree-Fock wavefunction, including Mulliken population analysis, multipole moments, and electrostatic fields.
- d) Automated geometry optimization to either minima or saddle points, and analytical or numerical differentiation to produce force constants, polarizabilities, and dipole derivatives. This feature can be used to develop minimum energy reaction paths along a complicated many dimensional potential energy surface.
- e) Correlation energy calculations using Møller-Plesset perturbation theory carried to second, third, or fourth order.
- f) Correlation energy calculations using configuration interaction (CI) with either all double excitations (CID) or all single and double excitations (CISD).
- g) Correlation energy calculations using coupled cluster theory with double substitutions (CCD).
- h) Correlation energy calculations using quadratic convergence SCF (QCSCF). This is a new highly efficient size-consistent method recently developed by Pople.
- i) Analytic computation of the nuclear coordinate gradient of the RHF, UHF, ROHF, GVB-PP, MP2, CID and RCISD energies.
- j) Computation of force constants (nuclear coordinate second derivatives), polarizabilities, hyperpolarizabilities, dipole derivatives, and polarizability derivatives either analytically or numerically.

- k) Harmonic vibrational analysis.
- l) Determination of intensities for vibrational transitions at the HF, MP2, and CI levels.
- m) Testing the SCF wavefunctions for stability under release of constraints.
- n) Correlated electron densities and properties.
- o) Minimum-energy pathway following from products to reactants through a transition state-intrinsic reaction coordinate finder.

2.2.2 GAMESS

A wide range of quantum chemical computations are possible using GAMESS (Reference 42), a refinement by M. Schmidt and S. Elbert of the original HONDO code (Reference 46).

The capabilities of this code include:

- a) Calculations of RHF/UHF/ROHF/GVB-SCF molecular wavefunctions.
- b) Calculations of multiconfiguration SCF (MCSCF) wavefunctions.
- c) Calculations of CI wavefunctions using the unitary group method.
- d) Optimization of molecular geometries using an energy gradient in terms of Cartesian or internal coordinates.
- e) Searches for potential energy surface saddle points.
- f) Tracing the intrinsic reaction path from a saddle point to reactants or products.
- g) Computation of normal modes and vibrational frequencies.
- h) Calculation of the following properties:
 1. dipole, quadrupole, and octupole moments
 2. electrostatic potentials
 3. electric field and electric field gradients
 4. electron density and spin density
 5. Mulliken and Lowdin population analysis
 6. localized orbitals by the Boys method
 7. virial theorem and energy components.

GAMESS is a synthesis, with many major modifications, of several programs. A large part of the program is from HONDO. For pure sp basis sets, the HONDO symmetry and supermatrix procedure has been adapted from GAUSSIAN 76 and GRADSCF integrals, both for the SCF and gradient parts. The GVB section is a heavily modified version of GVBONE. A Boys localization algorithm is implemented from a heavily modified version of Streitweiser's QCPE program.

The CI module is based on Brooks and Schaefer's unitary group program which was modified to run within GAMESS, using a Davidson eigenvector method written by S. T. Elbert. The MCSCF module is a Newton-Raphson procedure, developed at NRCC, based on the unitary group CI package. The intrinsic reaction coordinate pathfinder was written at North Dakota State University.

2.2.3 CADPAC

The Cambridge Analytic Derivatives Package (CADPAC) (Reference 47) is a group of programs which has been under development at Cambridge University, UK. It originated as a version of Dupuis and King's HONDO program. From its initial state as an SCF gradient package for closed-shell and UHF wavefunctions, this program has been extensively modified with many of the old features being enhanced and many new features being added. The input data is now in free format with a 'keyword' system, to make the program easier to use. The integral routines use essentially the same methods as those in HONDO, *being based on the Rys polynomial method*, but have been extended to cover f-functions. These routines have also been vectorized to take advantage of the much greater availability of supercomputers such as the Cray in recent years. The SCF programs are by now a blend of techniques, but still contain a few features from the initial HONDO program, particularly in the way symmetry is handled. There have been many modifications to improve efficiency and the addition of level-shifting and damping techniques and the implementation of the DIIS method to aid convergence. A high-spin open-shell SCF program, and a completely general open-shell SCF program have also been included.

The gradient routines have been considerably altered from those in the original HONDO, the method having been changed to one which is more efficient and easier to extend to higher-order derivatives. These routines also work for f-functions. The original program's capabilities for the calculation of force-constants by numerical differentiation of gradients and for the optimization of geometries remain essentially intact. However there is now a choice of two optimization algorithms with the inclusion of Schlegel's method.

In addition to the above modifications a range of extra facilities were developed. These included a more powerful method of calculating one-electron properties and analyzing molecular charge distributions, and various 'post-SCF' stages, beginning with a 4-index transformation.

These new sections include Møller–Plesset perturbation theory for total energies and molecular properties, and coupled Hartree–Fock calculations of molecular polarizabilities. The polarizability routines can calculate dynamic properties at real or imaginary frequencies, and obtain dispersion coefficients. It is also possible to use CHF theory to obtain the perturbations due to nuclear displacements. These can be used to obtain, analytically, all the dipole and quadrupole moment derivatives of a molecule. They also form part of the most important addition to the package, the section which calculates analytic second derivatives of the energy. This is a powerful technique whose speed and accuracy represents a considerable improvement over numerical differentiation.

The capabilities of the latest CADPAC code (Version 4) include:

- a) the evaluation of one- and two-electron integrals over contracted cartesian gaussian basis functions of type s, p, d, or f.
- b) SCF calculations for closed shell, open-shell, UHF and generalized open-shell techniques.
- c) calculation of one-electron properties for these types of wavefunction, including a distributed multipole analysis.
- d) calculation of the gradients of the SCF energy.
- e) use of the gradients for automatic geometry optimization, and for the calculation of force constants by numerical differentiation. There is a choice of two optimization algorithms.
- f) transformation of the integrals from the atomic orbital to the molecular orbital basis.
- g) Møller–Plesset perturbation theory calculations to third order in the energy and second order in the one-electron properties.
- h) coupled Hartree–Fock calculations of polarizabilities, including frequency dependence, and magnetizabilities.
- i) coupled Hartree–Fock calculations of the perturbation due to nuclear displacements.
- j) calculation of the dipole and quadrupole moment derivatives.
- k) calculation of the second derivatives (force constants) of the energy by analytic methods.
- l) analytic calculations of polarizability derivatives.
- m) calculation of infrared and Raman intensities, and the study of vibrational circular dichroism.

- n) calculation of MP2 gradients, dipole moment derivatives, polarizabilities and force constants using analytic algorithms.
- o) spin-projected UHF MP2 energies

2.2.4 HONDO

The HONDO program, (Reference 46) originally developed by Dupuis and King at NRCC has recently been refined and updated by M. Dupuis at IBM-Kingston (Reference 48).

The following features are available in the present version (HONDO 7) of the program:

- a) Single configuration self-consistent-field wavefunctions (closed shell RHF, spin unrestricted UHF, restricted open shell ROHF), generalized valence bond GVB and general multiconfiguration self-consistent-field MCSCF wavefunctions, and configuration interaction CI wavefunctions can be calculated.
- b) The electron correlation correction to the energy of closed shell RHF wavefunctions can be calculated by means of Møller-Plesset (MP) perturbation theory applied to second-, third-, and fourth-order (with or without the effects of triple excitations).
- c) The effective core potential approximation can be used.
- d) Optimization of molecular geometries using the gradient of the energy with respect to nuclear coordinates is possible with all but the CI and MP wavefunctions. Optimization can be carried out in the cartesian space or in the internal coordinate space with the possibility of freezing some cartesian or internal coordinates.
- e) The force constant matrix in the cartesian space, and the vibrational spectrum, including infrared and Raman intensities, can be calculated with all but the CI and MP wavefunctions.
- f) Calculation of the dipole moment and polarizability derivatives with respect to the nuclear coordinates is possible, for use with a previously calculated force constant matrix. The force constant matrix can be transformed to the internal coordinate basis.
- g) Transition state structures can be determined with all but the CI and MP wavefunctions by taking advantage of the energy gradients.
- h) The 'Intrinsic Reaction Coordinate' (IRC) pathway can be determined with all but the CI and MP wavefunctions by taking advantage of the energy gradients.
- i) Molecular energies for several points on a potential energy surface can be calculated in a single run.

- j) Non-gradient optimization of basis function exponents is possible. The source code can be modified to carry out optimization of other non-linear parameters, for example, contraction coefficients and geometrical parameters.
- k) The following electronic properties can be extracted from the wavefunction:
 - 1. dipole moment
 - 2. quadrupole moment
 - 3. Mulliken population, bond order and valency analyses
 - 4. spin density maps
 - 5. electron density maps
 - 6. electrostatic potential maps
 - 7. localized orbitals via Boys' method
 - 8. static dipole polarizability
 - 9. static first and second hyperpolarizabilities.
- l) The potential due to finite point charges for a classical representation of an environment, or a uniform electric field can be incorporated into the one-electron Hamiltonian.

2.2.5 COLUMBUS

The COLUMBUS code (Reference 49 and 50) is a continuing development based on a joint project at Ohio State University (I. Shavitt), University of Karlsruhe (R. Ahlrichs), and Argonne National Laboratory (R. Shepard). The unique features of this code are the incorporation of relativistic or non-relativistic core potentials to permit analysis of heavy atom molecular systems and the inclusion of a sophisticated CI package based on the unitary group approach of Shavitt (Reference 51). The basic programs included in the COLUMBUS code are as follows.

1. AO Integrals

This is R. Pitzer's version of the integral package from HONDO with partial vectorization of auxiliary integral routines. This package can handle up to g-functions.

2. Integral Transformation

The transformation algorithm is written over all the orbitals which constitute a shell, using contraction coefficients defined over the primitive basis functions. Limited vectorization is possible over the innermost loops for dyadic operations.

3. SCF Gradients

These routines are based on the HONDO version but include checks on integral symmetry to avoid operations over zero or near zero elements. At this time, only a first derivative analysis has been included.

4. SCF Energy

The SCF routines are typical of those found in the molecular structure codes. They incorporate level shifting, damping and the incorporation of Pulay's DIIS convergence acceleration procedure.

5. MCSCF Analysis

The MCSCF package is due to R. Shepard and incorporates extensive vectorization. The output vectors can be taken directly from this package and transferred to the CI program.

6. Multireference Direct CI

This set of routines is based on the graphical representation of the unitary group approach (GUGA) for constructing a CI wavefunction. This code differs from conventional CI in that a matrix representation of the hamiltonian is not explicitly computed. The unitary group approach can be much more efficient in most applications since $\sim 80\%$ of the hamiltonian matrix elements are usually zero but must still be included. This leads to the storage and diagonalization problems associated with large, sparse matrices. However, little work has been done on analysis of excited states with the same molecular symmetry as the ground state. An approach that looks promising is to define an approximate vector corresponding to the excited state wavefunction and to iteratively improve upon this solution using the direct CI contraction. The uncertainties in the procedure are applications to situations where degeneracies or near-degeneracies arise. Further studies of this case are in progress.

2.3 Spin-Projected Unrestricted Hartree-Fock Method

The unrestricted Hartree-Fock (UHF) method developed by Pople and Nesbet (References 52 and 53) yields the best single-determinant approximation to the exact wavefunction for an atomic or molecular system. Such a wavefunction incorporates correlation by allowing orbitals of different spin to adjust to spatially different forms, thus breaking the symmetry restrictions of the conventional (RHF) method (References 54 and 55). It is necessary, however, to project from such a wavefunction, a properly antisymmetrized spin and angular momentum state in order to define eigenstates and eigenenergies corresponding to observable spectroscopic states.

Let $|\alpha\rangle, |\beta\rangle$ refer to the doubly-occupied molecular orbitals (MO's), ϕ_α, ϕ_β . Let $|\gamma\rangle, |\delta\rangle, |\tau\rangle$ refer to the singly occupied MO's. We assume that all MO's have been subjected to a

transformation to orthogonal form. Let $C_{\gamma\delta}$ be the coefficient associated with the permutation $\gamma \leftrightarrow \delta$ (this permutation is (-1) times the overlap of the permuted spin eigenfunction with the original spin eigenfunction), and adopt the convention $C_{\gamma\gamma} = -1$. Then the expectation value of the nonrelativistic Hamiltonian

$$\mathfrak{H} = \sum_i U(i) + \sum_{i < j} V(i, j) \quad (22)$$

is given by

$$\begin{aligned} \langle \mathfrak{H} \rangle = & 2 \sum_a \langle a | U | a \rangle + \sum_\gamma \langle \gamma | U | \gamma \rangle + 2 \sum_{a\beta} \langle a\beta | V | a\beta \rangle \\ & - \sum_{a\beta} \langle a\beta | V | \beta a \rangle + 2 \sum_{\alpha\gamma} \langle \alpha\gamma | V | \alpha\gamma \rangle - \sum_{\alpha\gamma} \langle \alpha\gamma | V | \gamma\alpha \rangle \\ & - \frac{1}{2} \sum_{\gamma\delta} \langle \gamma\delta | V | \gamma\delta \rangle + \frac{1}{2} \sum_{\gamma\delta} C_{\gamma\delta} \langle \gamma\delta | V | \delta\gamma \rangle \end{aligned} \quad (23)$$

where i, j refer to electron numbers, a, β, γ, δ etc., refer to MO's and the sums run over all a, β, \dots

The equations for determining the optimum MO's can be derived from the following variational form

$$\delta \left[\langle \mathfrak{H} \rangle - 2 \sum_{a\beta} \epsilon_{a\beta} \langle a | \beta \rangle - \sum_{a\beta} (\epsilon_{\gamma a} \langle a | \gamma \rangle + \epsilon_{a\gamma} \langle \gamma | a \rangle) - \sum_{\gamma\delta} \epsilon_{\gamma\delta} \langle \gamma | \delta \rangle \right] = 0 \quad (24)$$

These equations are

$$(U + 2J_c - K_c + J_o - \frac{1}{2}K_o)|\alpha\rangle = \sum_{\beta} \epsilon_{\beta\gamma}|\beta\rangle + \frac{1}{2} \sum_{\delta} \epsilon_{\delta\alpha}|\delta\rangle \quad (25)$$

$$(U + 2J_c - K_c + J_o)|\gamma\rangle + \sum_{\delta} C_{\gamma\delta}|\langle\delta|V|\gamma\rangle\delta\rangle = \sum_{\beta} \epsilon_{\beta\gamma}|\beta\rangle + \sum_{\delta} \epsilon_{\delta\gamma}|\delta\rangle \quad (26)$$

where

$$|\langle\delta|V|\gamma\rangle\delta\rangle = \int d\vec{r} \phi_{\delta}(\vec{r})V(\vec{r}, \vec{r})\phi_{\gamma}(\vec{r})\phi_{\delta}(\vec{r})$$

$$\langle W|V|W'\rangle = \int d\vec{r} W^+(\vec{r})V(\vec{r}, \vec{r})W'(\vec{r}) \quad (27)$$

$$J_c = \sum_{\beta} \langle\beta|V|\beta\rangle \quad J_o = \sum_{\delta} \langle\delta|V|\delta\rangle$$

$$K_c|W\rangle = \sum_{\beta} |\langle\beta|V|W\rangle\beta\rangle \quad K_o|W\rangle = \sum_{\delta} |\langle\delta|V|W\rangle\delta\rangle$$

Left-multiplying Equation (25) by $\langle\gamma|$ and Equation (26) by $\langle\alpha|$, these equations can be combined to yield

$$\epsilon_{\gamma\alpha} = \sum_{\delta} (2C_{\gamma\delta} + 1)\langle\gamma\delta|V|\delta\alpha\rangle \quad (28)$$

Noting that

$$\sum_{\gamma} C_{\gamma\tau} \langle\delta\tau|V|\tau\gamma\rangle = \sum_{\tau} C_{\delta\tau} \langle\delta\tau|V|\tau\gamma\rangle, \quad (29)$$

Equations (25) and (26) can be recast as follows. From Equation (25),

$$\frac{1}{2} \sum_{\delta} \epsilon_{\delta\alpha} |\delta\rangle = \frac{1}{2} M |\alpha\rangle$$

with

(30)

$$M = \sum_{\delta\tau} (2C_{\delta\tau} + 1) |\delta\rangle \langle \tau| \langle \delta| V | \tau \rangle$$

From Equation (26),

$$\sum_{\beta} \epsilon_{\beta\gamma} |\beta\rangle = \sum_{\beta\tau} (2C_{\gamma\tau} + 1) |\beta\rangle \langle \beta\tau| V | \delta\gamma\rangle = O_c M^{\dagger} |\gamma\rangle$$

(31)

with

$$O_c = \sum_{\beta} |\beta\rangle \langle \beta|; \quad O_o = \sum_{\delta} |\delta\rangle \langle \delta|$$

(32)

Using Equations (31) and (32) in (25) and (26), we find

$$(U + 2J_c - K_c + J_o - \frac{1}{2} K_o - \frac{1}{2} M) |\alpha\rangle = \sum_{\beta} \epsilon_{\beta\alpha} |\beta\rangle$$

(33)

$$(U + 2J_c - K_c + J_o - \frac{1}{2} K_o + \frac{1}{2} M^{\dagger} - O_c M^{\dagger}) |\gamma\rangle = \sum_{\delta} \epsilon_{\delta\gamma} |\delta\rangle$$

(34)

Finally, Equations (33) and (34) can be rearranged to yield the same Hermitian operator on the left-hand side with the resulting definition of the one-electron eigenenergies for the closed and open-shell eigenstates:

$$\epsilon_a' = \langle a | U + 2J_c - K_c + J_o - \frac{1}{2} K_o | a \rangle \quad (35)$$

$$\epsilon_\gamma' = \langle \gamma | U + 2J_c - K_c + J_o - \frac{1}{2} K_o + \frac{1}{2} M^\dagger | \gamma \rangle \quad (36)$$

Equations (35) and (36) represent the correct one-electron energy expressions for the spin-projected eigenstate.

This formalism has been developed to extend the conventional HF method to include split-shell correlation and proper spin and symmetry projections. It is being incorporated into a computer program using gaussian-type orbitals (GTO's) as the elementary basis functions. A crucial feature of this method is that dissociation always follows the lowest energy pathway thereby permitting a proper description of bond formation and breakage. In contrast, RHF or MC-SCF methods often exhibit improper dissociation character or exhibit size inconsistencies owing to correlation energy changes in going from molecular geometries to separated atom-molecule or atom-atom dimensions.

2.4 Transition Probabilities

The electronic and vibrational-rotational wavefunctions of a pair of states can be used to calculate transition probabilities. If two molecular states are separated in energy by an amount $\Delta E_{nm} = hc\nu$ (h = Planck's constant, c = velocity of light, ν = frequency in wave numbers), the semi-classical theory of radiation (References 57 and 58) yields for the probability of a spontaneous transition from an upper state n to a lower state m

$$A_{nm} = \frac{4}{3} \frac{\Delta E_{nm}^3}{\hbar^4 c^3} \frac{S_{nm}}{g_n} \quad (37)$$

Here A_{nm} is the Einstein coefficient for spontaneous transition from level $n \rightarrow m$, g_n is the total

degeneracy factor for the upper state

$$g_n = (2 - \delta_{\sigma, \Lambda'}) (2S' + 1) (2J' + 1) \quad (38)$$

and S_{nm} is the total strength of a component line in a specific state of polarization and propagated in a fixed direction. A related quantity is the mean radiative lifetime of state n defined by

$$\frac{1}{\tau_n} = \sum_{m < n} A_{nm} \quad (39)$$

the summation being over all lower levels which offer allowed connections. The intensity of the emitted radiation is

$$I_{nm} = \Delta E_{nm} N_n A_{nm} \quad (40)$$

where N_n is the number density in the upper state n . This analysis assumes that all degenerate states at the same level n are equally populated, which will be true for isotropic excitation. The total line strength S_{nm} can be written as the square of the transition moment summed over all degenerate components of the molecular states n and m :

$$S_{nm} = \sum_{i,j} |M_{ji}|^2 \quad (41)$$

where j and i refer to all quantum numbers associated collectively with upper and lower electronic states, respectively.

In the Born-Oppenheimer approximation, assuming the separability of electronic and nuclear motion, the wavefunction for a diatomic molecule can be written as

$$\psi'_{VJM\Lambda} = \psi'_{el}(\vec{r}, R) \psi'_v(R) \psi_{JM\Lambda}(\theta, \chi, \phi) \quad (42)$$

where $\psi_{el}^i(\vec{r}, R)$ is an electronic wavefunction for state i at fixed internuclear separation R , $\psi_v(R)$ is a vibrational wavefunction for level v , and $\psi_{J\Lambda M}(\theta, \chi, \phi)$ refers to the rotational state specified by electronic angular momentum Λ , total angular momentum J and magnetic quantum number M . The representation is in a coordinate system related to a space-fixed system by the Eulerian angles (θ, χ, ϕ) . The transition moment M_{ji} can be written, using the wavefunction given by Equation (42), as

$$M_{ji} = \int \psi_{v'J'\Lambda'M'}^j \{ \vec{M}^e + \vec{M}^n \} \psi_{v''J''\Lambda''M''} d\tau_e d\tau_v d\tau_r \quad (43)$$

The subscripts e , v and r refer to the electronic, vibrational and rotational wavefunctions and \vec{M}^e and \vec{M}^n are the electronic and nuclear electric dipole moments, respectively. Integration over the electronic wavefunction, in the Born-Oppenheimer approximation, causes the contribution of the nuclear moment \vec{M}^n to vanish for $i \neq j$. The electronic dipole moment can be written (References 57 and 58) in the form

$$\vec{M}^e = - \sum_k e \vec{r}_k' = - \left\{ \sum_k e \vec{r}_k \right\} \cdot \vec{\Phi}(\theta, \chi, \phi) \quad (44)$$

where the primed coordinates refer to the space fixed system, the coordinates \vec{r}_k refer to a molecule-fixed system and $\vec{\Phi}(\theta, \chi, \phi)$ is a group rotation tensor whose elements are the direction cosines related to the Eulerian rotation angles (θ, χ, ϕ) . Using bracket notation, Equations (43) and (44) can be combined to yield for the transition moment

$$M_{ji} = M_{iv''J''\Lambda''M''}^{jv'J'\Lambda'M'} = \langle j | v' | - \sum_k e \vec{r}_k | iv'' \rangle \cdot \langle J' \Lambda' M' | \vec{\Phi}(\theta, \chi, \phi) | J'' \Lambda'' M'' \rangle \quad (45)$$

The matrix elements $\langle J' \Lambda' M' | \vec{\Phi}(\theta, \chi, \phi) | J'' \Lambda'' M'' \rangle$ determine the group selection rules for an allowed transition and have been evaluated for many types of transitions (References 59-61). Summing Equation (45) over the degenerate magnetic quantum numbers M' and M'' we have from

Equation (41)

$$S_{nm} = S_{mv''J''\Lambda''}^{nv'J'\Lambda'} = \mathcal{J}_{J''\Lambda''}^{J'\Lambda'} P_{mv''}^{nv'} \quad (46)$$

where $\mathcal{J}_{J''\Lambda''}^{J'\Lambda'}$ is the Honl - London factor References (62 and 63) and

$$P_{mv''}^{nv'} = \sum_{i,j} |\langle jv' | - \sum_k e\vec{r}_k | iv'' \rangle|^2 \quad (47)$$

is the band strength for the transition. Combining Equations (38), (40) and (46), we have for the intensity of a single emitting line from upper level n:

$$I_{nm} = i_{mv''J''}^{nv'J'} = \frac{4}{3} N_{J'} \frac{[\Delta E_{mv''J''}^{nv'J'}]^4 S_{mv''J''\Lambda''}^{nv'J'\Lambda'}}{\hbar^4 c^3 \omega_n (2J' + 1)} \quad (48)$$

where $N_{J'}$ is the number density in the upper rotational state J' and $\omega_n = (2 - \delta_{o\Lambda}) (2S' + 1)$ is the electronic degeneracy. Taking an average value of $\Delta E_{mv''J''}^{nv'J'}$ for the whole band, Equation (48) can be summed to yield the total intensity in the (v', v'') band:

$$I_{mv''}^{nv'} = \sum_{J', J''} I_{mv''J''}^{nv'J'} = \frac{4}{3} N_{v'} \frac{[\overline{\Delta E_{mv''}^{nv'}}]^4 P_{mv''}^{nv'}}{\hbar^4 c^3 \omega_n} \quad (49)$$

where $N_{v'} = \sum_{J'} N_{J'}$ is the total number density in the upper vibrational level v' and where we make use of the group summation property

$$\sum_{J''} \mathcal{J}_{J''\Lambda''}^{J'\Lambda'} = (2J' + 1) \quad (50)$$

Comparing Equations (40) and (49) we have for the Einstein spontaneous transition coefficient of the band (v', v'')

$$A_{mv''}^{nv'} = \frac{4}{3} \frac{[\overline{\Delta E_{mv''}^{nv'}}]^3 P_{mv''}^{nv'}}{\hbar^4 c^3 \omega_n} \quad (51)$$

Similarly, the lifetime of an upper vibrational level v' of state n can be written

$$\frac{1}{\tau_n} = \sum_{m < n} \sum_{v''} A_{mv''}^{nv'} \quad (52)$$

where the summation runs over all v'' for each lower state m . Equation (51) can be cast in the computational form

$$A_{mv''}^{nv'} (\text{sec}^{-1}) = \frac{(21.41759 \times 10^9)}{\omega_n} [\Delta E_{mv''}^{nv'} (\text{a.u.})]^3 p_{mv''}^{nv'} (\text{a.u.}) \quad (53)$$

where $\Delta E_{mv''}^{nv'}$ and $p_{mv''}^{nv'}$ are in atomic units. It is also often convenient to relate the transition probability to the number of dispersion electrons needed to explain the emission strength classically. This number, the f -number or oscillator strength for emission, is given by

$$f_{nm, v'v''} = \frac{mc^3 h^2}{2e^2 [\Delta E_{mv''}^{nv'}]^2} A_{mv''}^{nv'} \quad (54)$$

The inverse process of absorption is related to the above development through the Einstein B coefficient. Corresponding to Equation (40), we have for a single line in absorption

$$\frac{I_{mn}}{I_v^0 \Delta x} = \int_{\text{line}(v''v'J''J')} K(\nu) d\nu = h\nu_{mn} N_m B_{mn} \quad (55)$$

where $K(\nu)$ is the absorption coefficient of a beam of photons of frequency ν and

$$B_{mn} = B_{mv''J''\Lambda''}^{nv'J'\Lambda'} = \frac{2\pi}{3\hbar^2 c} \frac{S_{mv''J''\Lambda''}^{nv'J'\Lambda'}}{\omega_m (2J'' + 1)} \quad (56)$$

is the Einstein absorption coefficient for a single line. Summing over all lines in the band (v'', v') , assuming an average band frequency, we obtain

$$\frac{I_{mv''}^{nv'}}{I_v^0 \Delta x} = N_{v''} \frac{2\pi}{3\hbar^2 c \omega_m} p_{mv''}^{nv'} \overline{\Delta E_{mv''}^{nv'}} \quad (57)$$

where $N_{v''} = \sum_{J''} N_{J''}$ is the total number density in the lower vibrational state v'' . Corresponding to Equations (53) and (54) we can define an f-number or oscillator strength for absorption as

$$f_{mn,v''v'} = \frac{2m\Delta\overline{E}_{mv''}^{nv'}}{3\hbar^2 e^2 \omega_m} p_{mv''}^{nv'} \quad (58)$$

In computational form, Equation (58) becomes

$$f_{mn,v''v'} = \frac{2}{3} \cdot \frac{\Delta\overline{E}_{mv''}^{nv'}(\text{a.u.})}{\omega_m} p_{mv''}^{nv'}(\text{a.u.}) \quad (59)$$

where $\Delta\overline{E}_{mv''}^{nv'}$ and $p_{mv''}^{nv'}$ are in atomic units. Combining Equations (51) and (54) and comparing with Equation (58), we see that the absorption and emission f-numbers are related by

$$f_{mn,v''v'} = \left(\frac{\omega_n}{\omega_m}\right) f_{nm,v'v''} \quad (60)$$

Some caution must be observed in the use of f-numbers given either by Equations (54) or (58); since both band f-numbers and system f-numbers are defined in the literature. The confusion arises from the several possible band averaging schemes that can be identified.

An integrated absorption coefficient (density corrected) can be defined from Equation (57) as

$$S_{v'',v'} = \frac{1}{P_c} I_{mv''}^{nv'} = N_{v''} B_{v'',v'} \left(1 - \exp \frac{-hc\nu_{v'',v'}}{kT}\right) h \frac{\nu_{v'',v'}}{P_c^2} \quad (61)$$

where the exponential factor corrects for stimulated emission. Equation (61) can be written in terms of the absorption f-number as

$$S_{v'',v'} = \frac{\pi e^2}{mc^2} \frac{N_{v''}}{P} \left(1 - \exp \frac{-hc\nu_{v'',v'}}{kT}\right) f_{mn,v''v'} \quad (62)$$

Using $hc/k = 1.43880 \text{ cm-K}$, we obtain a computational formula for the integrated absorption coefficient as $S_{v'',v'}(\text{cm}^{-2}\text{atm}^{-1}) =$

$$2.3795 \times 10^7 \left(\frac{273.15}{T(\text{K}^\circ)} \right) \left(\frac{N_{v''}}{N_T} \right) \left(1 - \exp \frac{1.43880 \nu_{v'',v'}(\text{cm}^{-1})}{T} \right) \cdot f_{mn,v'',v'} \quad (63)$$

The total integrated absorption is found from

$$S_{\text{TOTAL}} = \sum_{v''} \sum_{v'} S_{v'',v'} \quad (64)$$

where, under normal temperature conditions, only the first few fundamentals and overtones contribute to the summations.

The developments given above are rigorous for band systems where an average band frequency can be meaningfully defined. Further approximations, however, are often made. For example, the electronic component of the dipole transition moment can be defined as

$$\mathfrak{R}_{ji}(\mathbf{R}) = \langle j | - \sum_{\mathbf{k}} e \mathbf{r}_{\mathbf{k}} | i \rangle \quad (65)$$

This quantity is often a slowly varying function of \mathbf{R} and an average value can sometimes be chosen. Equation (47) can then be written approximately in factored form as

$$p_{mv'',v'}^{nv'} = q_{v'',v'} \sum_{i,j} |\mathfrak{R}_{ji}(\bar{\mathbf{R}})|^2 \quad (66)$$

where $q_{v'',v'}$, the square of the vibrational overlap integral, is called the Franck-Condon factor.

\mathfrak{R}_{ji} is evaluated at some mean value of the internuclear separation \mathbf{R} . In addition, it is sometimes possible to account for a weak \mathbf{R} -dependence in $\bar{\mathbf{M}}^e$ by a Taylor series expansion of this quantity about some reference value, $\mathbf{R}_{a\beta}$ usually referred to the (0, 0) band. We have,

$$\mathfrak{R}_{ji} = \mathfrak{R}_{ji}^{a\beta} \left[1 + a(\mathbf{R} - \mathbf{R}_{a\beta}) + b(\mathbf{R} - \mathbf{R}_{a\beta})^2 + \dots \right] \quad (67)$$

Substituting into Equation (67) and integrating yields

$$p_{mv'}^{nv'} \approx q_{v'v''} \sum_{ij} |\mathfrak{D}_{ji}^{u\beta} [1 + a(\overline{R_{v'v''} - R_{a\beta}}) + b(\overline{R_{v'v''} - R_{a\beta}})^2 + \dots]|^2 \quad (68)$$

where

$$\overline{R_{v'v''} - R_{a\beta}} = \frac{\langle v' | (R - R_{a\beta}) | v'' \rangle}{\langle v' | v'' \rangle} \quad (69)$$

is the R-centroid for the transition and

$$\overline{(R_{v'v''} - R_{a\beta})^2} = \frac{\langle v' | (R - R_{a\beta})^2 | v'' \rangle}{\langle v' | v'' \rangle} \quad (70)$$

is the R^2 -centroid. Note that this last term differs (to second order) from the square of the R-centroid. An alternate procedure can be developed by evaluating Equation (65) at each R-centroid,

$\bar{R}_{v'v''}$. Then

$$p_{mv'}^{nv'} \approx q_{v'v''} \sum_{ij} |\mathfrak{D}_{ji}(\bar{R}_{v'v''})|^2 \quad (71)$$

Equation (71) assumes that the vibrational wavefunction product $\psi_{v'}\psi_{v''}$, behaves like a delta function upon integration,

$$\psi_{v'}\psi_{v''} = \delta(R - \bar{R}_{v'v''})\langle v' | v'' \rangle \quad (72)$$

The range of validity of Equation (71) is therefore questionable, particularly for band systems with bad overlap conditions such as oxygen Schumann-Runge. The range of validity of the R-centroid approximation has been examined by Frazer (Reference 64).

The final step in calculating transition probabilities is the determination of $\mathfrak{D}_{ji}(R)$, the electronic dipole transition moment, for the entire range of internuclear separations, R , reached in the vibrational levels to be considered. This can be expressed in terms of a CI expansion as

$$\mathfrak{D}_{ji}(R) = \sum_{\mu\nu} c_{\mu}^j * c_{\nu}^i \langle \psi_{\mu}(R) | \bar{M}^e | \psi_{\nu}(R) \rangle \quad (73)$$

where c_{μ}^j and c_{ν}^i are coefficients for ψ_{μ}^j and ψ_{ν}^i , respectively.

An analysis similar to that yielding Equations (10) and (11) gives

$$\langle \psi_{\mu}(R) | \tilde{M}^c | \psi_{\nu}(R) \rangle = \sum_p \epsilon_p \langle \theta_{Ms} | O_S P | \theta_{Ms} \rangle \left\langle \prod_{k=1}^n \psi_{\mu k}(\tilde{r}_k, R) | \tilde{M}^c P | \prod_{k=1}^n \psi_{\nu k}(\tilde{r}_k, R) \right\rangle \quad (74)$$

The spatial integral in Equation (74) reduces to one-electron integrals equivalent to overlap integrals, and the evaluation of Equation (74) can be carried out with any of the standard *ab initio* programs such as DLATOM or GAMESS. Programs for evaluating $\mathfrak{R}_{ji}(R)$ in Equation (73) have been developed at UTRC and examples of their application have appeared in the literature (Reference 65).

For perturbed electronic systems, the transition dipole moment will have a strong R-dependence and R-centroid or other approximations will be invalid. A direct evaluation of Equation (47) would therefore be required using the fully-coupled system of electronic and vibrational wavefunctions to properly account for the source of the band perturbations.

SECTION 3

DISCUSSION AND RECOMMENDATIONS

Several broad surveys of advanced propulsion systems have been undertaken within the past ten years (References 66–70). The objectives of these surveys were to identify new sources of propulsion energy, ranging from novel energetic chemical species to advanced concepts such as antimatter annihilation (References 71 and 72). Within the framework of advanced propulsion systems deriving their energy source from non-nuclear chemical reactions, we can consider several categories of energetic species. They include:

- 1) ordered (or metallic) forms of matter which at conventional temperatures and pressures are molecular solids. Metallic hydrogen and ammonium are examples.
- 2) free radicals, either atomic or molecular in nature, that are stabilized against recombination by condensation and immobilization on noble gas matrices held at very low (4 K) temperatures. Atomic hydrogen, beryllium monohydride (BeH) and the hydroxyl (OH) radical are examples in this category.
- 3) electronically excited metastable atoms or molecules that are stabilized against radiative decay by externally applied electric, magnetic or radiation fields, or by an intrinsic field within a condensed phase of such material which acts as a barrier to their decay. Metastable atoms, such as $\text{He}^*(^3\text{S})$ or $\text{N}^*(^2\text{D})$, and metastable molecules, such as $\text{H}_4(^1\text{A}_1)$, $\text{He}_2(a^3\Sigma_u^+ \text{ or } ^5\Sigma_g^+)$, $\text{HeH}_2(^1\text{A}'\text{II})$ and $\text{H}_2(\text{B}^1\Sigma_u^+)$, are examples in this category that would constitute significant energy sources (> 1000 kJoule/mol).
- 4) strained molecules with high positive heats of formation. This is an important class of molecules which are really isomeric forms of conventional chemical species but are structurally prevented from relaxation to their lowest energy state or to decomposition by significant activation barriers on their potential energy surface. Examples in this category include vinylidene, several structures of Li_mH_n , cyclopropene, aziridine, azetidine and covalent azides or azide-like structures. Hypervalent compounds such as NF_5 or ClOF_5 would also be included in this category.

Ordered or metallic states of solids that are normally molecular have been extensively studied both experimentally and theoretically (References 73–76). Detailed quantum mechanical studies of several crystalline forms of metallic hydrogen have been carried out which yield 200–300 kJoules of energy above the normal solid molecular form. This translates into an available specific impulse in excess of 1200 seconds. However, the derived thermodynamic properties from these calculations suggest that external pressures of the order of several megabars would be required to

form the metallic phase. Since this pressure requirement is approximately one order of magnitude higher than has ever been achieved (except possibly by thermonuclear explosions), there is currently very little active research in this area. There appears to be little more that theoretical studies can contribute until significant advances in high pressure technology are achieved.

The concept of using stabilized free radicals as a propulsion energy source must be tempered by an assessment of the maximum specific impulse that can be derived from such systems. The bond energy of molecular hydrogen (436 kJoule) translates into an available specific impulse in excess of 1800 seconds, provided there are no constraints on the density of hydrogen atoms that could be formed and stabilized. The available specific impulse drops dramatically when other free radicals are considered. As an example, atomic oxygen atoms, stabilized in their ground 3P state, would yield approximately 600 seconds and most other dissociated molecules, stabilized as free radicals, are not sufficiently energetic to yield a specific impulse greater than the baseline value of 389 seconds available from H_2/O_2 . The early research efforts in free radical stabilization are reviewed in the book by Bass and Broida (Reference 10). An analysis by Rosen (Reference 77) on the prospects for stabilizing hydrogen atoms in significant concentrations, and the recent experimental studies on spin polarized hydrogen reported by Hess (Reference 78), suggest that storage of high densities of hydrogen atoms will be difficult to achieve. The very low temperatures required (< 4 K) to minimize recombination processes and the dilute surface storage requirements are serious obstacles when viewing these materials as chemical propellants. An experimental program was carried out for AFRPL by this Center in an effort to stabilize light element atoms at 77 K (Reference 79). The maximum concentration that was realized was well below that required for consideration as a possible propulsion system. Attempts to stabilize H atoms in various host matrices all indicated that no significant reaction barrier to atomic recombination could be achieved. These observations, coupled with a thermodynamic analysis indicating that only stabilized light element atoms would offer any significant improvement over conventional fuel types, suggest that this area may be of limited value for consideration as an advanced fuel type. Recently, however, (References 80–82), the idea of trapping ions or free radicals in a noble gas matrix has been reexamined under the High Energy Density Matter (HEDM) program. The basic concept is that noble gas hydride species such as Ar_nH^+ are stable and may offer a route to hydrogen atom stabilization. Another possibility is to store metal atoms interstitially in a dilute host matrix such as hydrogen. The intermolecular separation of H_2 molecules in the solid phase is large compared to many light metal atom radii. Both theoretical and experimental studies of these mechanisms should be further pursued.

The above analysis, however, suggests that research efforts for identifying high energy non-nuclear fuels should probably be concentrated in the remaining categories of metastable species and highly strained molecular compounds. Since the number and type of compounds that

might be formed is potentially very large, it would be helpful if certain criteria could be established to focus both theoretical and experimental studies into areas where there is a significant higher probability of forming high energy molecular species. A systematic study to establish such criteria for screening diatomic and triatomic molecules that could be formed from the first 18 elements was performed by this Center for AFRPL in the mid-sixties (Reference 83). The electronic structure and energy content of those molecules that showed high performance potential as energy sources in a chemical propulsion system were then examined using state-of-the-art quantum mechanical valence bond programs. These calculations were pioneering at the time but are admittedly crude in comparison to results obtainable today from currently available techniques, as outlined in the Mathematical Background section of this report.

This research program for AFRPL, which surveyed some 2000 electronic states of 171 diatomic molecules and over 10,000 electronic states of 324 triatomic molecules that could be formed using atoms ranging from H to Ar, did establish certain fundamental criteria for estimating performance potential. The foremost guideline involves the molecular weight of the energetic species. The specific impulse of chemical propulsion systems can be estimated on the basis of the properties of the major exhaust products, i.e. the effective species which determine the available energy content of the reaction. To a good approximation we find:

$$I_{sp} = 295 \left[\frac{\Delta H}{W} \right]^{1/2} \quad (75)$$

where I_{sp} is the specific impulse (sec), ΔH is the difference between the combustion chamber and exhaust enthalpies (kcal) and W is the weight of the propellant (gm), as determined by the effective number of moles of gaseous products and the stoichiometry of the propellant system. For many propellant combinations, it has been shown that the quantity, $\Delta H/n_e$, which represents the change of enthalpy per mole of gas phase species, can be related to the heat of reaction of the propellant or, more simply, to the available energy content. If hydrogen gas is chosen as the working fluid, a universal plot of specific impulse as a function of molecular weight of the energetic species, with energy content as a parameter, can be constructed. This is illustrated in Figure 1 where we have also labeled the specific impulse available from both conventional fuels and those proposed as high energy fuels.

It is clear from Figure 1 that the molecular weight of the "energy carrying" species in a chemical propulsion system is the overriding factor for our evaluation of expected performance. Taking metastable $\text{He}_2^+ [a^3\Sigma_u^+]$ as an example (labeled 15 on Figure 1), we find a maximum available I_{sp} of ~ 1370 seconds. The chemically similar metastable Ne_2^+ , however, only yields a maximum I_{sp} of ~ 630 seconds, mainly due to the detrimental effects of increased molecular

HYDROGEN CONTENT VARIED TO OPTIMIZE IMPULSE (1000 – 14.7 psia)

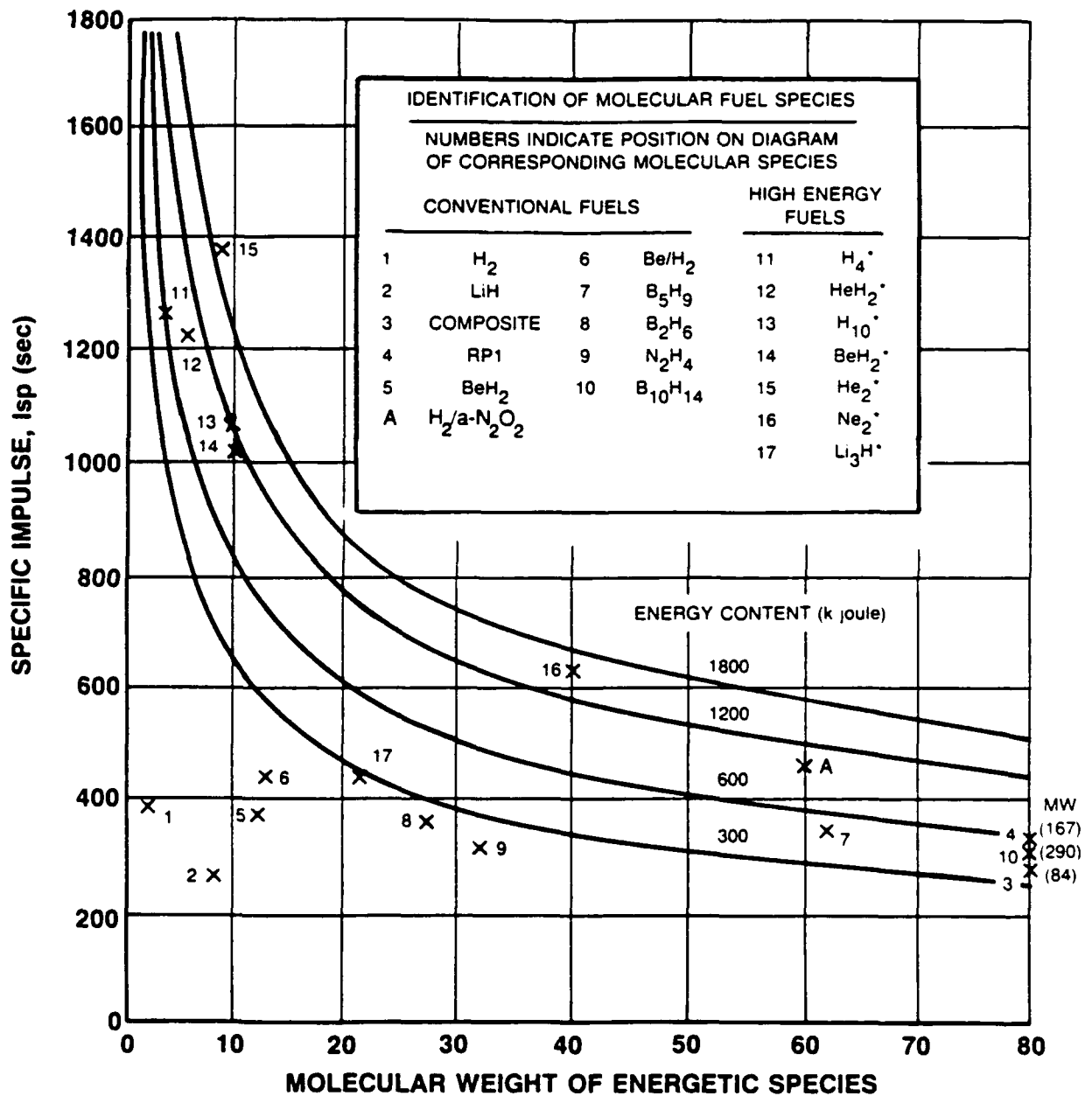


Figure 1. Specific Impulse Obtainable from Fuel/Oxidant Energy Release with Hydrogen as a Working Fluid

weight. Those species labeled as high energy fuels on Figure 1 are all capable of delivering specific impulses greater than ~ 1000 seconds except for Ne_2^+ and Li_3H^+ , which is just at baseline I_{sp} (450 sec), again mainly from molecular weight considerations. Using an available energy content of ~ 1200 kJoules which, except for He_2^+ , is a realistic upper limit to the energy that can be stored in an electronically excited metastable state of a molecule, we find a molecular weight cut-off of ~ 30 if a 50% improvement in performance is desired over that available from conventional fuel types. This is obviously not a hard number for all metastable species but gives us guidance to the type of compounds that should be considered.

In the category of strained molecules with positive heats of formation, we can establish an appropriate upper limit to the available energy of such compounds based on their lowest ionization potential. The reasoning here is that isomeric forms of a given compound, such as Li_3H , which have energy in excess of their lowest ionization potential, would constitute autoionizing or continuum electronic states with lifetimes dictated by intrinsic quantum mechanical decay pathways (spin-recoupling, electron autodetachment, etc.). Considering only compounds formed from atoms through carbon, we again find (He being an exception) a molecular weight cut-off of ~ 30 for a 50% improvement in I_{sp} over conventional fuels. A more conservative (and realistic) estimate of the molecular ionization potentials (600 kJoules) would indicate that emphasis should be placed on studies of energetic species with molecular weight of 20 or less. This clearly rules out all hydrocarbons and even most boron compounds if significant increases in chemical propulsion performance are desired. We are thus led to consider, as primary candidates, those molecular structures that can be formed from hydrogen through boron which have a molecular weight of ~ 30 or less. The chemistry of boron compounds has been extensively studied (References 84 and 85) and only those energetic compounds containing at most three boron atoms would meet our criteria for a significant improvement in available specific impulse.

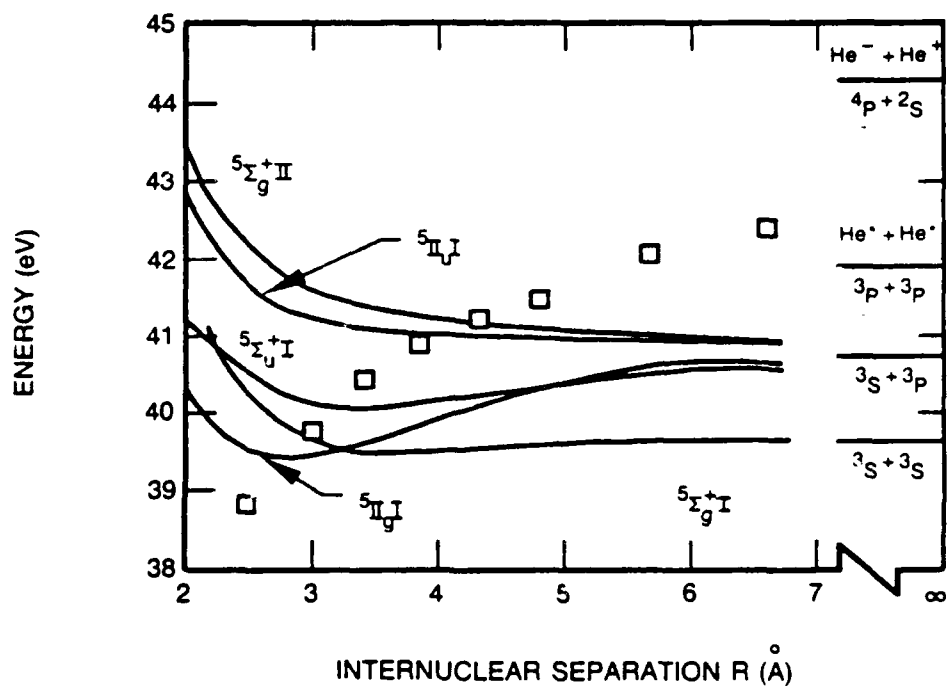
This preliminary analysis does not rule out the possible utility of higher molecular weight species as advanced fuel types. Our studies of both advanced fuels and oxidizers, under this research program, have indicated (to date) that the identification of an advanced fuel with performance significantly better than H_2 , using O_2 as an oxidizer, may prove to be difficult. The C_{2v} structure of, Li_3H may offer some improvement and is described in more detail below. However, our studies of oxidizers have resulted in the identification of the covalent azide, FN_3 , and the azide-like molecule, $\alpha\text{-N}_2\text{O}_2$, as powerful new oxidizers when used as replacement species for ammonium perchlorate (AP) in typical solid propellant formulations. In addition, theoretical studies indicate that the hypervalent structure, NF_5 , is vibrationally stable with a positive heat of formation for the D_{3h} (trigonal bipyramid) structure. Although previous attempts to synthesize this molecule have been unsuccessful, our calculations shed some light on synthesis routes that may be promising. Our preliminary studies of high energy species have thus led us to

the conclusion that significant improvements in solid formulations may be possible through the development of advanced oxidizers.

Turning next to an analysis of electronically excited metastable molecules, we note that a theoretical study of such species has been performed by this Center for AFRPL (Reference 83). This study and more recent investigations acknowledge that no mechanism has yet been found that would prevent radiative decay of such molecules in a time span of a few seconds or less. Recently, however, Zmuidzinas has proposed (Reference 13) that spin-polarized triplet helium atoms could be stabilized by forming the metastable $^5\Sigma_g^+$ state of He_2^* which exhibits no first order decay process to the autoionizing continuum of $\text{He}_2^+ + e$ or to ground state helium atoms.

In an effort to more fully understand the chemistry of such excited states we recently initiated a series of calculations of the low-lying quintet states of He_2^* using extended CI wavefunctions. A previous *ab initio* study by Garrison, Miller and Schaefer (Reference 15) had indicated that the $^5\Sigma_g^+$ molecular state of He_2^* , arising from the interaction of two $^3\text{S}(2s)\text{He}^*$ atoms, exhibits 0.07 eV stability with no long range repulsive barrier. In Figure 2 we outline the results of our recent study. The low-lying $^5\Sigma_g^+$ quintet state of He_2^* arises from the $\text{He}^* ^3\text{S}(2s) + \text{He}^* ^3\text{S}(2s)$ asymptote while the low-lying $^5\Sigma_u^+$, $^5\Pi_u$, $^5\Pi_g$ and $^5\Sigma_g^+ \text{II}$ states arise from the $\text{He}^* ^3\text{S}(2s) + \text{He}^* ^3\text{P}(2p)$ asymptote. All of these molecular states are modified by interactions with the quintet $^5\Sigma_g^+$, $^5\Sigma_u^+$, $^5\Pi_g$ and $^5\Pi_u$ components of the ionic states arising from the $\text{He}^+ [^4\text{P}^*(2s2p)] + \text{He}^+ [^2\text{S}(2s)]$ asymptote. We find that the $^5\Pi_g$ state is actually the lowest molecular state among this group and would act to completely predissociate the weakly bound $^5\Sigma_g^+$ state. A further analysis of possible decay mechanisms for this low-lying $^5\Pi_g$ state indicates that a maximum radiative lifetime of $\sim 10 \mu\text{sec}$ could be expected for this metastable system. Thus stabilization of metastable $\text{He}^* [^3\text{S}(2s)]$ atoms by quintet molecular state formation is no more likely than by formation of the lowest $a^3\Sigma_u^+$ excited state of He_2^* .

We are led to the conclusion that simple stabilization of electronically excited atoms through molecule formation is unlikely. However, it might be possible to utilize the changed chemical characteristics of an excited atom or molecule to form a new molecular structure which represents a local point of stability on the ground state potential energy surface. Illustratively, we have the following example in Figure 3.



ENERGY SCALE IS GIVEN IN ELECTRON VOLTS (1 eV = 96.54 kJoules/mol) AND IS RELATIVE TO He [¹S (1s²)] + He [¹S (1s²)] = 0. THE IONIC CURVE LABELED BY THE SQUARES HAS THE He⁻ [⁴P] + He⁺ [²S] DISSOCIATION ASYMPTOTE.

Figure 2. Low-Lying Quintet States of He₂⁺

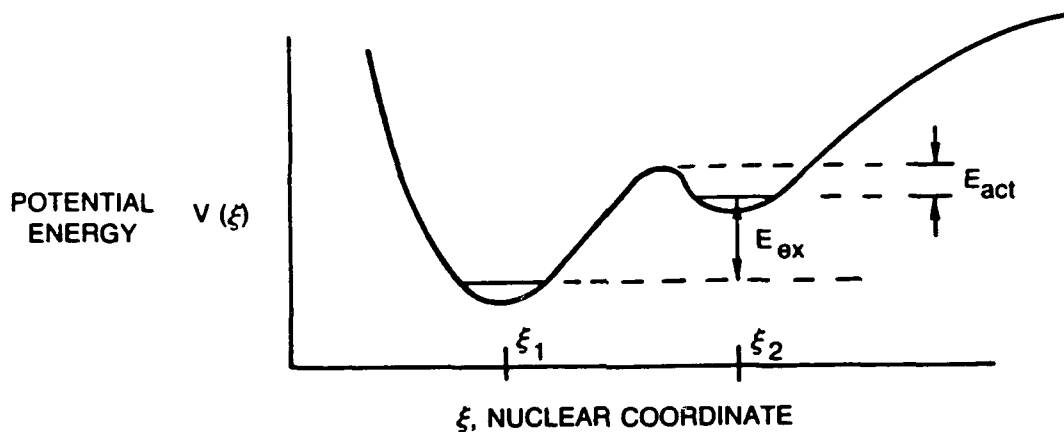


Figure 3. Generalized Reaction Surface

Here the most stable molecular configuration corresponds to ξ_1 whereas the system at ξ_2 represents an isomeric form of the molecule with extra energy, E_{ex} and which is stable against decay to the lowest state by the presence of an activation barrier, E_a . The crucial questions are: how high is the activation barrier in any system and how much extra energy can be stored in the system stabilized at this local minimum. The loss of molecules from the system at ξ_2 can be realized by tunneling (if E_a is small) or by extra internal energy as vibrations or rotations which would exceed E_a . The ideal system would have a large E_{ex} (high energy storage) and a large E_a (high barrier for decay) with one or more vibrational levels possible at the geometry represented by ξ_2 . It is tempting to call these structures isomeric conformations of the most stable ground state arrangement of atoms, but that label is usually reserved for regions ξ_2 that can be reached by symmetry operations (rotations, reflections) of the molecule. Often the molecular conformation at ξ_2 represents a high symmetry point on the potential energy surface. It is crucial to examine such points to determine if they represent true minima or if they are saddle points which are unstable against some mode of internal molecular motion. We show below that the H_4 (tetrahydrogen) system is a classic example of a local minima on a ground potential energy surface which, in fact, represents an unstable saddle region.

Structural and thermodynamic studies of molecules which correspond to conformations represented by the region ξ_2 have been carried out under the present contract. To date, calculations have mainly focused on four types of compounds:

- 1) light element C_{3v} and C_{2v} structures (H_4 , Li_3H , LiH_3 , Li_4) which represent advanced fuel types
- 2) halogen azides and azide-like structures (FN_3 , $FNCO$, CO_3 , HN_3 , $FNBF$, $a-N_2O_2$) which represent advanced oxidizers

- 3) cyclic boron structures (B_3H_3 , B_2H_2NH) which are analogous to strained ring hydrocarbons cyclopropylene (C_3H_4) and ethyleneimine (C_2H_5N)
- 4) hypervalent molecules (NF_5 , PF_5), which exhibit high oxidization states.

We summarize below our theoretical studies in these four areas and suggest new avenues of research based on our experience under the present contract.

3.1 Light Element High Symmetry Structures

3.1.1 H_4

Our initial theoretical studies of advanced fuel types were focused on the energy content and stability of the H_4 (tetrahydrogen) system. The simple H_4 system has been the subject of many quantum chemical studies (Reference 86). Until recently, it was thought that the only binding in the ground state was due to the weak van der Waals interaction of two H_2 molecules (Reference 87) although several workers have suggested the existence of bound excited states (Reference 88). In particular, Nicolaides, Theodorakopoulos, and Petsalakis (References 89 and 90) have predicted the existence of a $^1A'$ bound excited state of H_4 in C_s symmetry, formed from the interaction of ground state H_2 with vibrationally excited $He_2^+ B^1\Sigma_u^+$. The calculations of Nicolaides, et al. show that this bound excited state of H_4 arises from an avoided crossing with the lowest $^1A'$ state. It is therefore likely that this first excited $^1A'$ state of H_4 is predisassociated through vibronic interaction with the ground state. In pure C_{3v} symmetry, the two $^1A'$ states discussed by Nicolaides, et al. correlate to the ground 1A_1 state and an excited 1E state. Because these states are of different symmetry, there is no avoided crossing in C_{3v} symmetry to stabilize the excited state, as there can be in the lower C_s symmetry. However, these same calculations also indicated that the ground state surface exhibits a local minimum in C_{3v} symmetry. Physically, this conformation may be viewed as arising from the binding of a hydride ion (H^-) to the stable H_3^+ trigonal ion. The purpose of our initial study was to examine this conformation in C_{3v} symmetry to determine the character of this minimum point.

Ab initio calculations on H_4 were performed with the 6s1p/4s1p basis of Nicolaides et al., and a more accurate 10s3p/5s3p basis. The 10s3p/5s3p basis consists of the 9s/4s contraction of Siegbahn and Liu (Reference 91) augmented by a diffuse s-type function (exponent 0.016). Using the Gaussian 82 system of programs (Reference 41), C_{3v} optimized structures were found at the SCF, MP2, and CISD levels of theory using the 6s1p/4s1p basis, and at the SCF and MP2 levels

using the 10s3p/5s3p basis. At each optimized geometry, a vibrational frequency analysis was performed. A summary of the results of these calculations is given in Table 1.

The most significant finding of these calculations was the existence of two imaginary vibrational frequencies, corresponding to an unstable vibrational mode of e symmetry. This result was obtained with both large and small basis sets, and at every level of theory. Using the 6s1p/4s1p basis set, an SCF calculation of the path of steepest descent from the C_{3v} optimized geometry was performed with the intrinsic reaction coordinate pathfinder of Schmidt, Gordon, and Dupuis (Reference 92) implemented in the GAMESS code. This calculation was performed with no symmetry constraints and indicated a monotonically decreasing path which dissociates into two H_2 molecules. We have concluded that the H_4 energy minima found in C_{3v} symmetry are not stable with respect to geometric perturbations which lower the spatial symmetry and that the ground 1A_1 state of H_4 in C_{3v} symmetry is not bound. Exploratory calculations were also performed in C_s symmetry to ascertain the possible existence of a bound state of H_4 in a slightly distorted pyramidal configuration. We were unable to locate such a state, as all of our optimizations tended either to dissociation or to the C_{3v} minimum described above.

Our stability analysis of $H_4(C_{3v})$ was obviously a disappointing result since, as shown on Figure 1, such a molecular species is estimated to yield a specific impulse of nearly 1300 seconds, based on our calculated bond energies relative to two ground state hydrogen molecules. Other structures of this type, however, are suggested by the similarity of H^- and Li^- . In Figure 4 we indicate several potential high-energy, light element C_{3v} molecular structures that result from systematic substitution of Li for H atoms. Li^- has an electron affinity of 0.62 eV, very similar to that of H^- (0.75 eV). In addition, Li_3 forms a stable molecule (Reference 93) with a binding energy of ~ 1.5 eV, relative to ground state $Li + Li_2$, whereas the neutral H_3 system is unstable at all geometries. This suggests a greater stability for the Li_3H species, but as shown in Figure 1, the increased molecular weight causes a penalty in the predicted I_{sp} .

3.1.2 Li_3H

Based on this analysis, the C_{3v} structure of Li_3H , which is the analog of tetrahydrogen with a Li_3^+ base, was examined using several basis sets and at the SCF and MP2 levels of theory. Calculations at both the SCF and MP2 level of theory, using several basis sets including diffuse orbitals are given in Table 2. These data indicate that this species is stable in all approximations that were examined. A diffuse basis (6-31++G*) was examined at the SCF level to insure that Li^- and H^- were accurately represented. However, the diffuse functions appear to have little

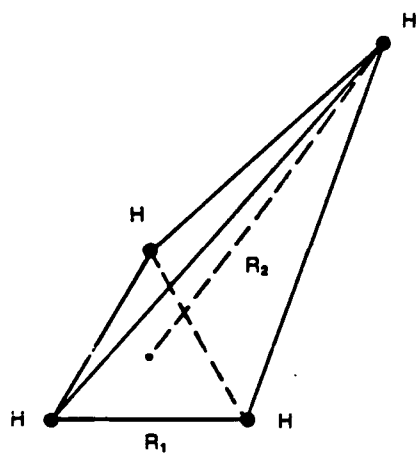
Table 1. *Ab Initio* Structure and Calculated Energy for H₄ in C_{3v} Symmetry

Theory	h	r	Energy	Frequencies			
				e	a ₁	e	a ₁
SCF/small	1.8784	0.8433	-1.982 831	2942i	1053	3069	3794
MP2/small	1.8094	0.8477	-2.035 124	3614i	1096	3010	3751
CISD/small	1.8048	0.8509	-2.049 161	4025i	1092	2962	3712
SCF/large	1.8634	0.8421	-2.000 761	2188i	1167	3101	3777
MP2/large	1.8170	0.8451	-2.063 595	2503i	1201	3051	3740

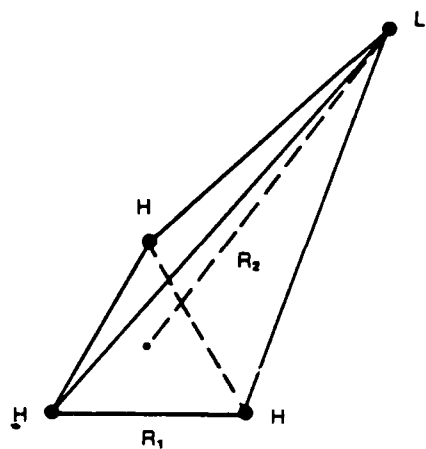
Energies (hartrees), distances (Å), frequencies (cm⁻¹)

h is the distance of the fourth proton from the center of the H₃ triangle of side r.

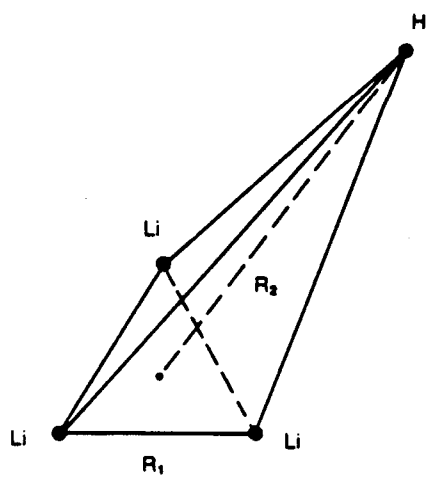
Small and large refer to the 6s1p/4s1p and 10s3p/5s3p basis sets, respectively. Note that the frequencies of the e modes are doubly degenerate.



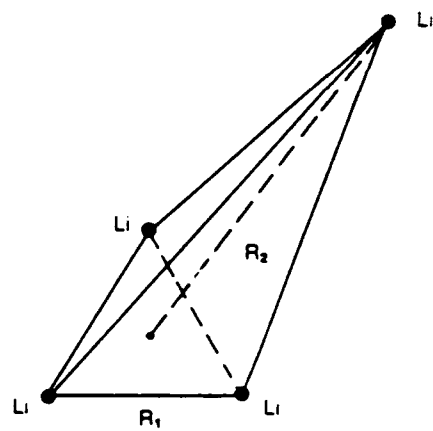
a) H_4 (UNSTABLE)



b) LiH_3 (UNSTABLE)



c) Li_3H (STABLE)



d) Li_4 (UNSTABLE)

Figure 4. High-Energy Light Element C_{3v} Molecular Structures

Table 2. Theoretical Results for Li_3H C_{3v} Structure

Level	Distances (\AA)		Energy (E_h)	Frequencies cm^{-1}			
	H-Li	Li-Li		e	a_1	e	a_1
SCF/6-31G*	1.9422	2.6461	-22.857 226	247	400	344	821
SCF/6-31++G**	1.9382	2.6532	-22.859 647	256	390	345	812
SCF/6-311G**	1.9082	2.5993	-22.867 477	291	390	421	837
MP2/6-31G*	1.9263	2.6391	-22.901 463	259	389	454	848
MP2/6-311G**	1.8558	2.5755	-22.958 672	280	387	511	853
MP2/6-311++G**	1.8571	2.5765	-22.959 007	281	387	510	849

effect in geometry optimization. The results for this basis were essentially the same as those with the double-zeta plus polarization basis sets. The optimized structure for Li_3H has a short pyramid height ($\sim 1.1 \text{ \AA}$) for the H^- anion above the Li_3^+ base. The structure thus somewhat resembles the NH_3 molecule. Although it is tempting to assign the ion pair state ($\text{Li}_3^+ + \text{H}^-$) interaction to the trigonal pyramidal structure (C_{3v}), because of its structural resemblance to the carefully studied H_4 species, the disparity in the Li-Li distance (at MP2/6-311++G**) between this structure (2.577 \AA) and Li_3^+ (3.001 \AA) suggests that the C_{3v} structure is not correctly characterized as an $\text{Li}_3^+ + \text{H}^-$ ion pair. This disparity was also noted by Talbi and Saxon (Reference 94), who suggested that the pyramidal structure is of mixed ion-pair and covalent character based on a wavefunction analysis.

Recently Cardelino, et al. (Reference 95) have shown that a kite-like C_{2v} structure for Li_3H is the ground state at the SCF level of theory. Calculations of this structure were carried out at both the SCF and MP2 level of theory, using 6-31G* and 6-311G** basis sets. The data are shown in Table 3 where the C_{2v} planar kite-like structure is, in fact, found to be lower in energy than the trigonal C_{3v} structure at both the SCF and MP2 level of theory. A harmonic frequency analysis indicates vibrational stability for this C_{2v} structure, which appears to be a Li atom bridged across the known, stable Li_2H molecule. The ionicity on the H atom is $\sim 18\%$ in this conformation as compared with $\sim 29\%$ for the trigonal C_{3v} structure. Since both of these structures exhibit stable vibrational frequencies, they probably represent different local minima on the same ground state surface. Preliminary studies of the transition state connecting these two structures have been carried out which indicate a slightly distorted (C_s) trigonal bipyramid, with nearly the same energy as the C_{3v} structure. Further detailed calculations of Li_3H are given in Appendix C where we illustrate that inclusion of zero-point energy requirements places the C_{3v} structure at the same level as the transition state, making the thermodynamic stability of the C_{3v} structure questionable. However, the C_{2v} structure is found to be stable, and represents the absolute ground state minima of the Li_3H surface.

The performance of the $\text{Li}_3\text{H}/\text{F}_2$ and $\text{Li}_3\text{H}/\text{O}_2$ bipropellant systems has been evaluated through specific impulse calculations. Calculations were performed for a combustion pressure of 800 psia and equilibrium flow through a nozzle having an exit-to-throat area ratio of 20:1. Two sets of calculations were performed in which the Li_3H was taken as the C_{2v} structure ($\Delta H_f = -3.49 \text{ kcal/mol}$) and as the C_{3v} structure ($\Delta H_f = +23.83 \text{ kcal/mol}$). As noted above,

Table 3. Theoretical Results for Li_3H C_{2v} Structure

Level	Distances (\AA)			Energy (E_h)		Frequencies cm^{-1}					
	H-Li	H-Li'	Li-Li	Li-Li'		b ₂	a ₁	b ₁	a ₁	b ₂	a ₁
SCF/6-31G*	1.7741	4.1741	2.5310	3.1923	-22.896 763	177	269	382	396	1039	1041
SCF/6-31++G**	1.7707	4.1799	2.5305	3.2018	-22.898 464	178	265	375	395	1034	1039
SCF/6-311G**	1.7327	4.1256	2.4832	3.1703	-22.906 001	178	263	385	399	1063	1092
MP2/6-31G*	1.7761	4.0994	2.5129	3.1092	-22.936 496	190	283	369	379	1036	1054
MP2/6-311G**	1.7164	4.0089	2.4596	3.0688	-22.992 986	192	279	377	399	1105	1080
MP2/6-311++G**	1.7160	4.0069	2.4601	3.0678	-22.993 238	192	279	377	398	1106	1079

only the C_{2v} structure appears to be vibrationally stable. The calculated performance curves are given in Figures 5 and 6, respectively, using F_2 and O_2 as oxidizers. It is seen that bipropellant combinations offer approximately a 10% improvement over the LiH/O_2 or LiH/F_2 systems. However, a significant increase in performance is available when Li_3H is used in a tripropellant formulation. The peak I_{sp} using O_2 and an optimum H_2 ratio ($Li_3H/H_2 = 0.5$), and assuming the C_{2v} structure for Li_3H , is 456 sec., which represents a 15 sec. improvement over the baseline H_2/O_2 system. Further studies, both theoretical and experimental synthesis, should be carried out on Li_3H .

Our previous argument concerning the stability of Li_3H would predict that the LiH_3 molecule should be unstable since back charge transfer into the H_3 ring would create an instability. In Table 4, we illustrate that this indeed is the case for LiH_3 , where two separate basis sets both yielded a structure with imaginary frequency components, i.e. a saddle geometry. Surprisingly, the Li_4 structure also has an imaginary frequency for the e-mode (triangle distortion), even with a diffuse (6-31+G*) basis set. The optimized geometry for Li_4 in C_{3v} yields bond lengths which suggest that a lower order symmetry is the true ground state. A search through the Carnegie-Mellon University Quantum Chemistry Archive verifies this idea, where the rhombus structure (D_{2h}) of Li_4 is found to be lower in energy. This D_{2h} structure is stable, relative to $Li_3 + Li$, by approximately 3.4 eV (Reference 96). Li_4 is thus probably less energetic as a fuel than $Li(s)$ or $LiH(s)$, and further studies of this molecule, considering the detrimental effect of molecular weight, are probably not of primary importance.

3.2 Halogen Azides and Azide-Like Structures

Calculations of hydroazoic acid (HN_3), fluorine azide (FN_3), fluorine isocyanate ($FNCO$), asymmetric dinitrogen dioxide ($a-N_2O_2$) and difluoraminoborane ($FNBF$) were carried out at several levels of theory to determine the most stable geometries of these azides and azide-like compounds. The results are summarized in Table 5 which indicates that a stable C_s structure exists for each of these compounds. A vibrational frequency analysis has also been carried out on each of these compounds. The results indicate a stable structure in $^1A'$ symmetry.

A comparison with experimental structures is shown in Table 5 for HN_3 and FN_3 . It is clear that very good agreement has already been achieved at the MP2 level of theory. Further studies are in progress at higher levels of theory, and with basis sets larger than the 6-31G* sets used in these initial studies.

Chamber pressure = 800 psia

$A/A^* = 20:1$

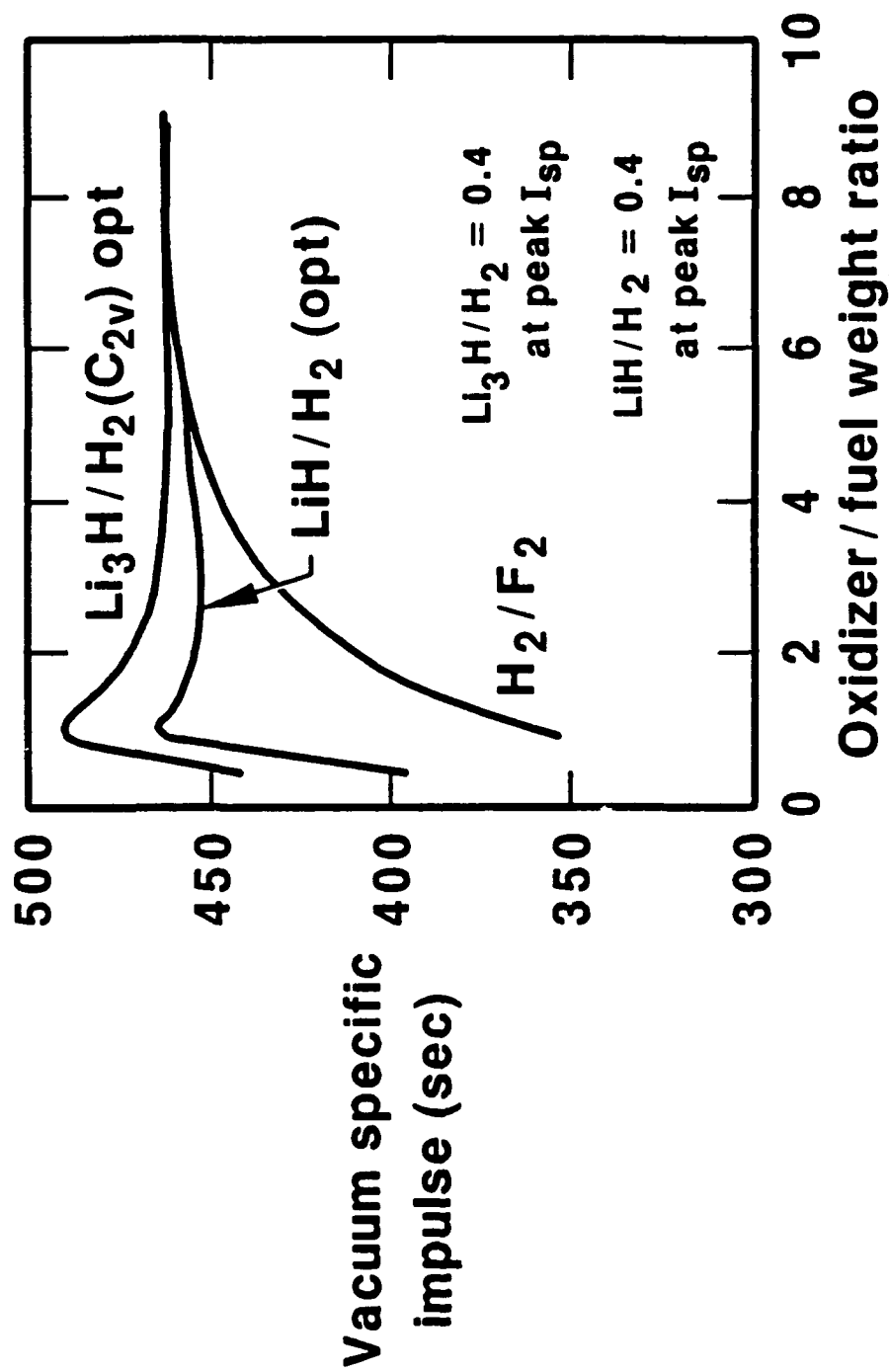


Figure 5. $\text{Li}_3\text{H}/\text{H}_2/\text{F}_2$ Vacuum Specific Impulse

Chamber pressure = 800 psia
 $A/A^* = 20:1$

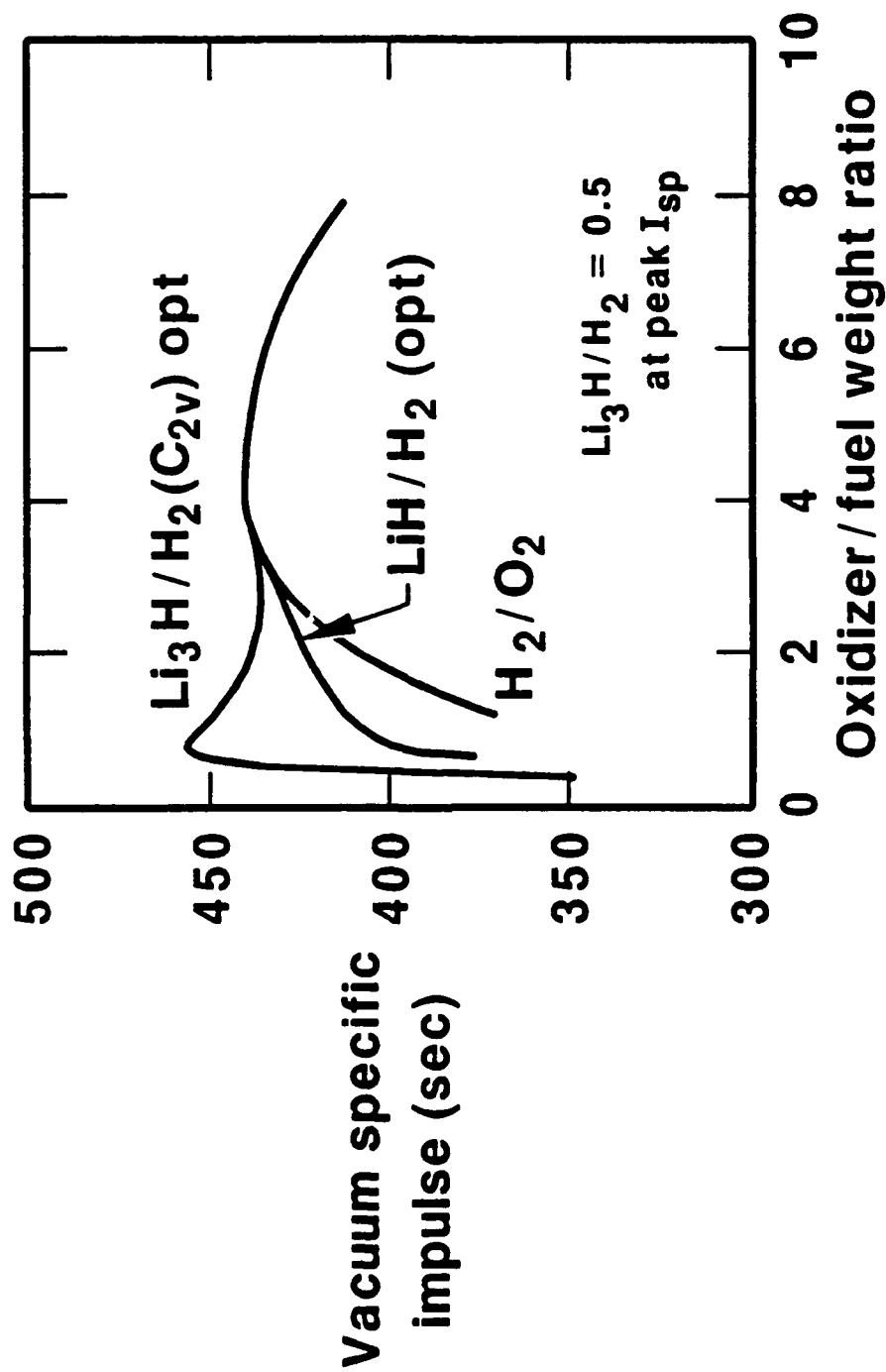


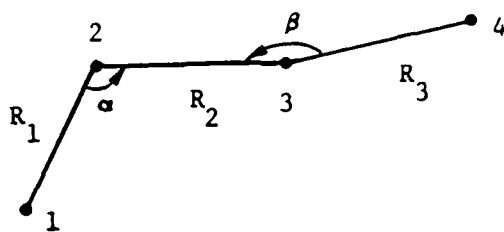
Figure 6. $\text{Li}_3\text{H}/\text{H}_2/\text{O}_2$ Vacuum Specific Impulse

**Table 4. *Ab Initio* Structure and Calculated Energy
for Li₄ and LiH₃ in C_{3v} Symmetry**

Theory	h	r	Energy	Frequencies			
				<i>e</i>	<i>α</i> ₁	<i>e</i>	<i>α</i> ₁
Li₄							
SCF/3-21G	3.1300	2.8191	-29.529616	218 <i>i</i>	193	285	356
SCF/3-21 + G	3.1304	2.8205	-29.530374	214 <i>i</i>	192	284	354
SCF/6-31G*	3.1439	2.8193	-29.722764	239 <i>i</i>	199	281	351
SCF/6-31 + G*	3.1526	2.8257	-29.724402	225 <i>i</i>	195	280	349
LiH₃							
SCF/3-21G**	1.5967	1.2216	-8.832136			Unstable (2)	
SCF/6-31G**	1.5954	1.2294	-8.887511			Unstable (2)	

Energies (hartrees), distances (Å), frequencies (cm⁻¹)

Table 5. Optimized Geometries of Azides



Compound	Theory	R_1 (Å)	R_2 (Å)	R_3 (Å)	α (deg)	β (deg)
HN ₃	SCF	1.0055	1.2381	1.0987	108.181	173.815
	MP2	1.0182	1.2502	1.1583	109.946	171.209
	EXP. ¹	1.012	1.240	1.134	112.65	(180.0)
FN ₃	SCF	1.3820	1.2536	1.0995	104.315	174.108
	MP2	1.4309	1.2799	1.1521	103.765	171.803
	EXP. ²	1.444	1.253	1.132	103.8	170.9
FNCO	SCF	1.3737	1.2387	1.1354	109.846	173.235
	MP2	1.4185	1.2622	1.1765	110.717	168.914
a-N ₂ O ₂	SCF	1.7574	1.2024	1.0844	103.966	179.506
	[MP2	1.5305	1.2272	1.1548	103.591	179.488]
	CISD	1.5817	1.2240	1.1072	102.867	179.344
FNBF	SCF	1.2993	1.2068	1.2871	180.000	180.000
	MP2	1.3394	1.2491	1.3069	154.650	169.291

() Assumed

[] ψ_0 not stable relative to rotation to complex form

¹ Reference 118

² Reference 98

3.2.1 a-N₂O₂

The most significant result of our studies of azide-like structures is the prediction of a stable, asymmetric C_s structure of dinitrogen dioxide with a characteristic IR frequency of 1206 cm⁻¹, corresponding to the N-O stretch. This frequency has previously been reported by Milligan and Jacox (Reference 97) in argon matrix studies of irradiated N₂O in the presence of alkali atoms and assigned to a possible N₂O₂ anion. It is not characteristic of other known nitrogen oxides. The calculated geometry for a-N₂O₂ is very similar to the structures of the isoelectronic species FN₃ and FNCO, which have recently been characterized both theoretically and experimentally (References 98 and 99).

The reaction of O[¹D] atoms with CO₂ is believed to yield the cyclic C_{2v} CO₃ structure (dioxirane), which has been found by Pople et al. to be more stable than the C_s structure (Reference 100). Therefore, calculations were also performed on the analogous C_{2v} structure of N₂O₂. Although it is a saddle point at the HF/3-21G level of theory, our HF/6-31G* calculations indicate that there is a vibrationally stable C_{2v} structure of N₂O₂ about 160 kJ/mol above the C_s structure. An optimized HF/6-31G* transition state for the C_{2v} to C_s rearrangement was found only 2 kJ/mol above the C_{2v} structure. Preliminary studies at the CISD level suggest that this barrier becomes even smaller when electron correlation effects are included. Therefore, it seems unlikely that the C_{2v} N₂O₂ structure will be formed in the O[¹D] + N₂O reaction.

There are also low-lying triplet states of N₂O₂, arising from O[³P] + N₂O and O₂[³Σ_g⁻] + N₂, and it is necessary to know their location to assess the stability of the singlet. A CISD/6-31G* energy calculation on the lowest ³A'' state, performed at the optimized geometry of the singlet, shows that the triplet lies 67 kJ/mol higher than the singlet. Since asymptotically the triplet surface lies lower than the singlet, further calculations are underway to characterize the crossing region and its effect on the stability of singlet a-N₂O₂.

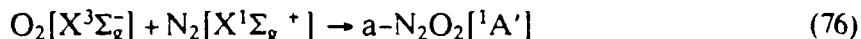
A series of Born cycle calculations were also carried out to determine the heat of formation of a-N₂O₂. The HF/6-31G result is ΔH_f^o = + 430.5 kJoule/mol. Additional studies were made at the HF/6-31G*, MP2/6-31G*, MP3/6-31G* and CISD/6-31G* levels of theory. The CISD calculations were corrected for size-consistency errors. The results are summarized as:

<u>Level of Theory</u>	<u>ΔH_f^o(a-N₂O₂), kJoule/mol</u>
HF/6-31G*	+ 559.3

MP2/6-31G*	+ 493.8
MP3/6-31G*	+ 507.6
CISD(SC)/6-31G*	+ 504.5

Excluding the HF result, which is predictably too high, we find an average value,

$\Delta H_f^\circ = + 504 \pm 10$ kjoule/mol, for the reaction:



This value for the heat of formation is for the gas phase species and must be reduced by the heat of sublimation (unknown). The energetics of the chemical synthesis of a-N₂O₂ are shown in Figure 7. Our calculated results for the equilibrium structure of N₂O₂ are given in Table 6.

The transition state of a-N₂O₂ corresponds to the activation energy required to decompose a-N₂O₂ into O₂[a¹Δ_g + b¹Σ_g⁺] + N₂[X¹Σ_g⁺]. The geometry corresponding to the transition state is: R_{OO} = 1.3980Å, R_{NO} = 1.4585Å, R_{NN} = 1.0745Å, with a calculated energy of E_{TS} (HF/6-31G*) = - 258.3244471 hartrees. This corresponds to an activation energy of +63.5 kjoule/mol which is typical of all the other known azide structures. The a-N₂O₂ dissociation pathway is illustrated in Figure 8.

In addition to these thermodynamic studies, an SCF stability analysis of asymmetric dinitrogen dioxide (a-N₂O₂) was carried out. An analysis of the stability of the RHF/6-31G* wavefunction for the equilibrium structure of a-N₂O₂ has shown it to be unstable with respect to a broken-symmetry UHF state. Using symmetric and antisymmetric combinations of the RHF HOMO and LUMO for the UHF guess, a broken-symmetry UHF solution was found at about 30 millihartrees lower energy than the RHF solution. This state showed severe spin contamination (< S₂ > = 0.851). A natural orbital decomposition of the UHF wavefunction revealed two orbitals with occupation numbers of 1.395 and 0.605, which were used as the pair orbitals in a GVB(1) calculation. This reorganization of the wavefunction gives an energy about 10 millihartrees below the RHF and retains pure singlet character. Geometry optimizations with the GVB(1)/6-31G* wavefunction have led to dissociation of the O-O bond, suggesting that further investigation would be required to determine the correct zero-order wavefunction for a-N₂O₂. A limited MCSCF/6-31G* calculation for a-N₂O₂, which correlated all three bond pairs (O-O, O-N, N-N) does yield a stable structure with geometry similar to that found in the CISD/6-31G* calculation in Table 6. Further studies of this system are clearly indicated.

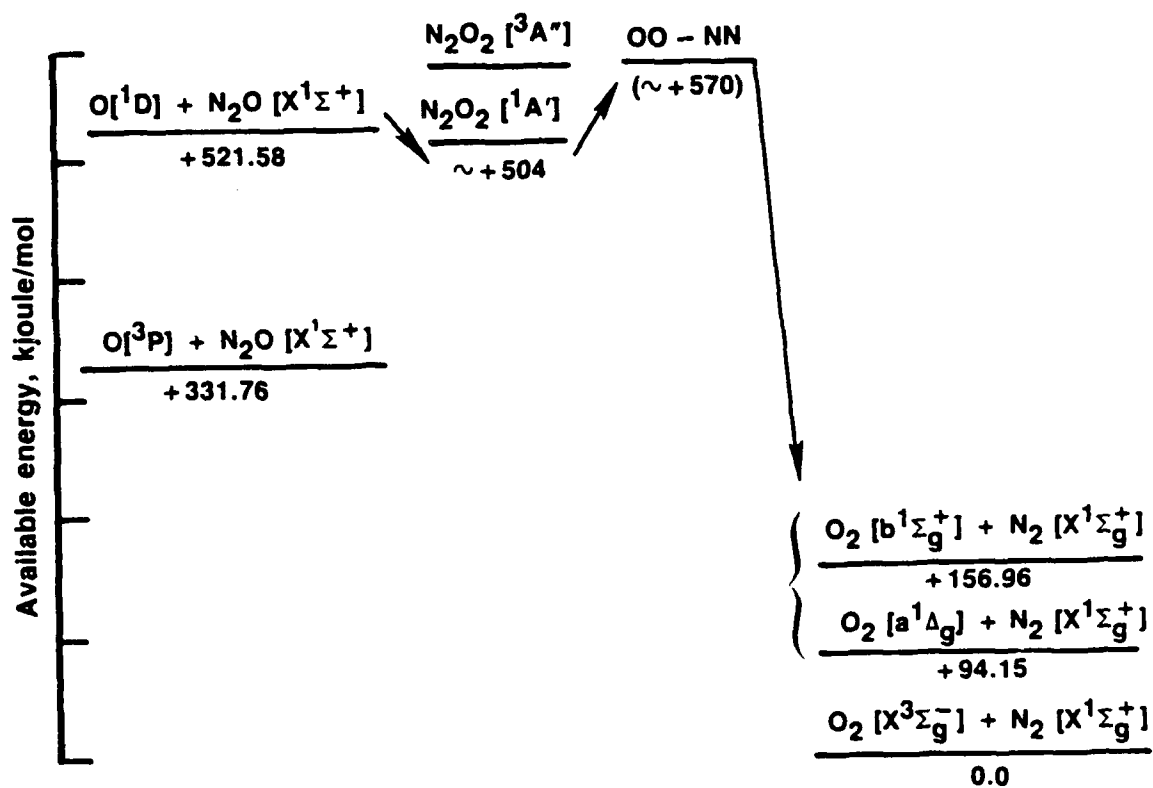


Figure 7. Energetics of the Chemical Synthesis of Dinitrogen Dioxide ($\alpha\text{-N}_2\text{O}_2$)

Table 6. N₂O₂ Theoretical Predictions

Level	C _s Structure [¹ A']		C _{2v} Structure [¹ A ₁]	
	HF/6-31G*	CISD/6-31G*		
Energy	HF/6-31G*	HF/6-31G*		HF/6-31G*
	-258.348 838	-258.932 499	-258.417 315	-258.287 006
Geometry				
R(O-O)	1.7574	1.5817	1.8014	R(O-O)
R(N-O)	1.2024	1.2240	1.1901	R(N-O)
R(N-N)	1.0844	1.1072	1.0787	R(N-N)
α	103.97	102.87	106.20	
β	179.51	179.34	179.62	
Vibrational Frequencies ^a				
a' N-N stretch	2677 (8.46)	2501	2656	a ₁ N-N stretch
a' O-N stretch	1262 (4.53)	1206	1282	a ₁ symmetric stretch
a' O-O stretch	697 (0.90)	648	707	a ₁ O-N-O scissor
a' O-N-N stretch	291 (2.08)	526	271	b ₂ O-N-O rock
a' O-O-N bend	188 (0.05)	227	169	b ₂ asymmetric stretch
a'' out-of-plane	648 (0.38)	580	655	b ₁ out-of-plane
				2203
				1178
				900
				670
				449
				515

^a HF/6-31G* IR intensities (in D²amu⁻¹°A⁻²) for the C_s structure are given in parenthesis following the corresponding frequencies.

Bond lengths are in angstroms, bond angles are in degrees, energies are in hartrees, and vibrational frequencies are in wavenumbers.

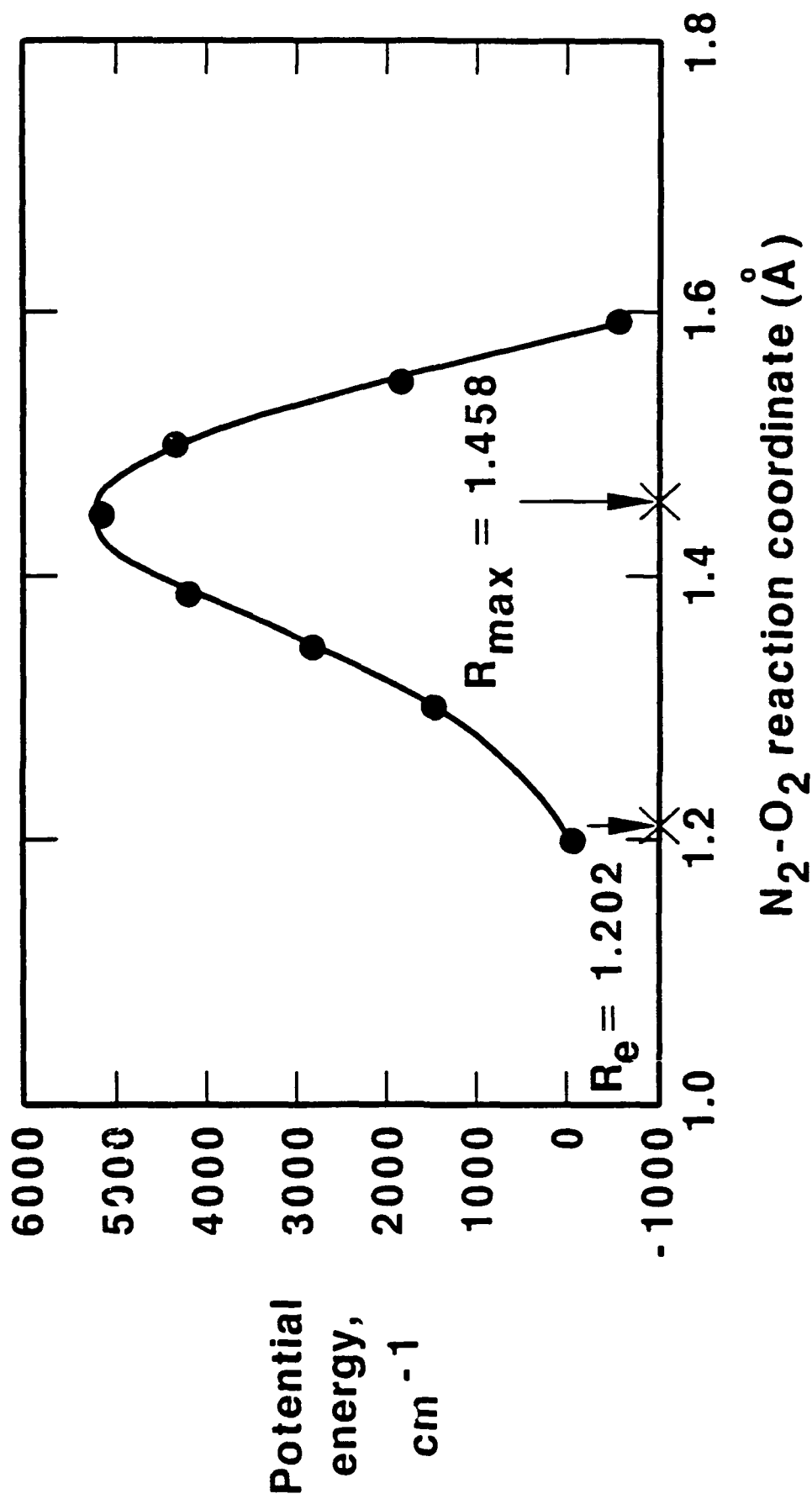
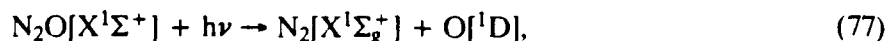


Figure 8. a- N_2O_2 Dissociation Pathway

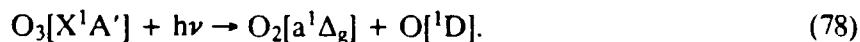
Finally, in Figure 9, we show the calculated vacuum specific impulse obtainable with a $\text{H}_2/\text{a-N}_2\text{O}_2$ propellant combination. The peak I_{sp} is ~ 455 sec., based on our present thermodynamic data. Metal loading would improve this performance and various hybrid combinations with $\text{a-N}_2\text{O}_2$ are presently being studied. As a direct replacement for ammonium perchlorate (AP) in a typical composite propellant, we find a specific impulse improvement of 1 sec/% replacement of AP by $\text{a-N}_2\text{O}_2$. Using typical binder loading, a 10 second improvement should be realizable with current mixes.

The molecule $\text{a-N}_2\text{O}_2$ appears to be a very attractive candidate as an advanced oxidizer and a patent disclosure has been initiated at UTRC for both the chemical formula and several proposed synthesis routes for this energetic species. Attempts to synthesize $\text{a-N}_2\text{O}_2$ by irradiation of N_2O in the liquid phase have been reported by Pritt (Reference 101). We have developed a route for synthesizing $\text{a-N}_2\text{O}_2$ using the reaction of oxygen atoms, prepared in their lowest [^1D] electronic state, with N_2O . In the following reactions, the molecules N_2O_2 , N_2 and O_3 are in the lowest or ground electronic state, O atoms are in the first excited [^1D] electronic state and the O_2 molecules are in the first excited [$\text{a}^1\Delta_g$] electronic state.

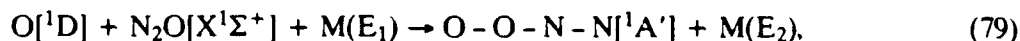
Oxygen atoms may be prepared in their lowest [^1D] electronic state by photolysis of N_2O :



or by the photolysis of O_3 :



The reaction is carried out in the presence of a nonreactive collisional species, e.g. He, Ne or N_2 , according to the reaction:



where M = nonreactive collisional species, and $\text{E}_2 - \text{E}_1$ = stabilization energy of $\text{O}-\text{O}-\text{N}-\text{N}$ in the lowest [A'^1] state. The function of the nonreactive collisional species is to kinetically carry off

Chamber pressure = 1000 psia
Exit pressure = 14.7 psia

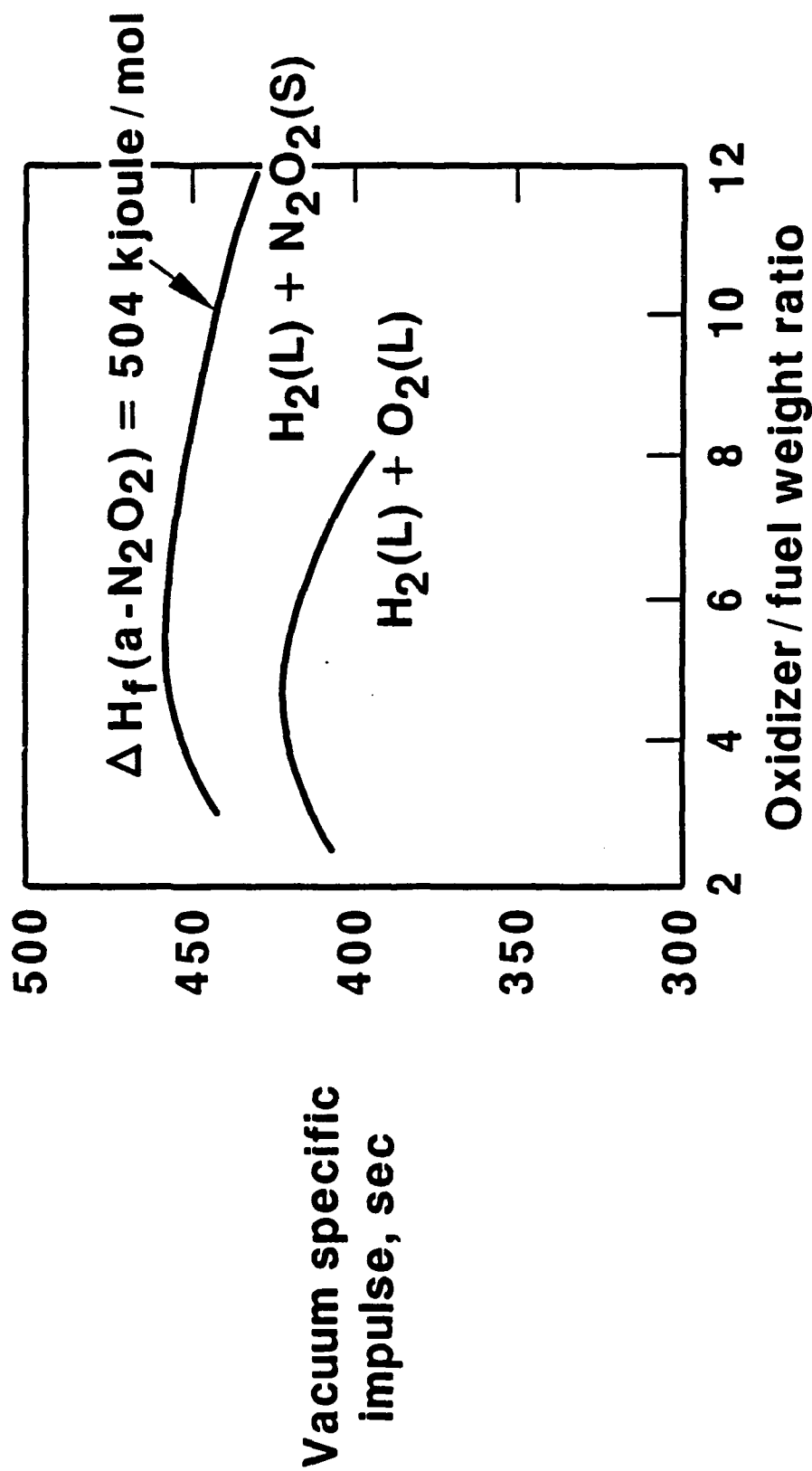


Figure 9. $\text{H}_2/\text{a}-\text{N}_2\text{O}_2$ Vacuum Specific Impulse

excess energy and allow the formation of a stable product. Reaction of the [^1D] oxygen atoms with the N_2O molecule would preferably be carried out in the the gas phase, however, liquid phase or *in situa* solid state formation are also possible.

Alternatively, $\alpha\text{-N}_2\text{O}_2$ could be formed by an exchange reaction of a type:



where $\text{M}'\text{O}$ is any species in which a [^1D] oxygen atom is chemically bound. Examples of suitable $\text{M}'\text{O}$ species include: HClO , HFO , ONF , ONCl and group IIA metal oxides where $\text{M}' = \text{Mg}$, Ca , Sn , or Ba .

Finally, the $\alpha\text{-N}_2\text{O}_2$ product is condensed to a storable form by cryogenically cooling the products of the gas phase reaction or by forming $\alpha\text{-N}_2\text{O}_2$ *in situa* on a surface held at cryogenic temperatures. The condensed product collected and stored at reduced, preferably cryogenic, temperatures.

Recently, Hinchey (UTRC) has attempted synthesis by matrix isolation of the products of laser dissociated N_2O . A unique IR signature has been identified in the $1220\text{--}1230\text{ cm}^{-1}$ region, very close to our predicted $\text{N-O}(\text{a}')$ stretch frequency. Further low temperature studies of $\alpha\text{-N}_2\text{O}_2$ are currently in progress to characterize this observed low temperature spectra. Additional theoretical studies should be carried out including characterization of the potential energy surface of $\alpha\text{-N}_2\text{O}_2$ in the $\text{N}_2\text{O}[\text{X}^1\Sigma^+] + \text{O}[\text{A}']$ reactant region, studies of singlet-triplet surface crossings and studies of the stability of $\alpha\text{-N}_2\text{O}_2$ against further reaction with oxygen atoms or molecules. The structure and energy of possible dimers of $\alpha\text{-N}_2\text{O}_2$ should also be examined.

3.2.2 FN_3

The FN_3 system is a HEDM material but it is also a possible chemical source for $\text{NF}[\text{a}^1\Delta]$. $\text{NF}[\text{a}^1\Delta]$ has the potential application of pumping the BiF short wavelength chemical laser. Calculations of the potential energy surfaces for FN_3 , both ground and excited states, have been initiated to compliment the experimental studies of this system currently being undertaken at Rockwell Science Center. The energetics and pathways for decomposition, and the prediction of

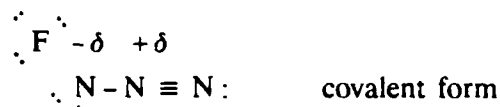
emission/absorption wavelengths are being studied both theoretically and experimentally. These studies were initiated by the needs of the Air Force Weapons Laboratory (AFWL) in Albuquerque to model the chemistry of FN_3 decomposition. Accordingly, the scope of this contract was expanded to include an in-depth study of the FN_3 system.

A detailed analysis of FN_3 has been carried out at geometries relevant to: a) the equilibrium ground $^1\text{A}'$ state, b) the transition state for decomposition to $\text{NF}[a^1\Delta + b^1\Sigma^+] + \text{N}_2[{}^1\Sigma_g^+]$, and c) the region of singlet-triplet crossing. The details of these three studies are outlined below:

a) Equilibrium Calculations

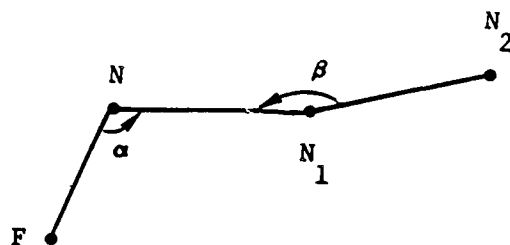
Ab initio theoretical calculations of the equilibrium structure and properties of fluorine azide (FN_3) have been performed using several standard basis sets and theoretical methods. SCF and MP2 calculations have been performed using the GAUSSIAN 86 and CADPAC programs. 6-in-6 CAS-MCSCF calculations have been performed using the GAMESS program. Gradient-optimized structures are reported in Table 7, and harmonic vibrational frequencies in Table 8. Also given for comparison are the recent experimental results of Christen, Mack, Schatte, and Willner (Reference 98). Good agreement with the experimental structure is found, with the correlated methods tending to correct the short SCF bond lengths. The harmonic vibrational frequencies are well described by MP2, except for the highest frequency mode, the terminal N-N stretch, which is predicted to be over 300 cm^{-1} too large. Systematic studies have shown MP2 vibrational frequencies are usually within 5% or so for small molecules (Reference 41). The 6-in-6 MCSCF calculation reduces this error by about 100 cm^{-1} , suggesting that the use of a single reference configuration is inadequate.

Physically, the short terminal N-N bond length and the observed dipole moment suggests the electronic structure of FN_3 may be described as



The MCSCF orbitals, CI coefficients and Mulliken populations suggest that admixtures of the

Table 7. FN_3 Equilibrium Geometry



Level	Alpha	Beta	NF	NN ₁	N ₁ N ₂	Energy	Dipole Moment
RHF/6-31G*	104.315	174.108	1.3820	1.2536	1.0995	-262.602488	1.60
RHF/DZP	104.345	174.592	1.3760	1.2638	1.1024	-262.661912	1.79
MP2/6-31G*	103.765	171.803	1.4309	1.2799	1.1521	-263.282402	1.68
MP2/DZP	103.836	172.133	1.4286	1.2928	1.1593	-263.385697	1.06
MP2/TZ2P	104.047	171.324	1.4268	1.2695	1.1382	-263.601495	
MC6/6-31G*	101.674	174.285	1.4630	1.2751	1.1154	-262.724363	1.99
exp	103.8	170.9	1.444	1.253	1.132		1.3

Bond lengths are in angstroms, bond angles are in degrees, energies are in hartrees and dipole moments are in Debyes.

Table 8. FN_3 Equilibrium Vibrational Frequencies

Level	$\mathbf{a'}$					$\mathbf{a''}$	ZPE
RHF/6-31G*	281	757	1045	1225	2386	606	3150
RHF/DZP	284	751	1027	1207	2350	596	
MP2/6-31G*	247	690	948	1153	2406	494	2969
MP2/DZP	247	677	930	1131	2383	471	
MC6/6-31G*	241	649	833	1021	2281	520	2773
exp	241	658	876	1090	2044	504	2706

Vibrational frequencies and zero point energies (ZPE) are in wavenumbers.

$$\begin{array}{l} \begin{array}{c} \cdot\cdot \\ \text{F} \\ \cdot\cdot \end{array} + \delta \quad -\delta \\ \quad \quad \quad \cdot\cdot \\ \quad \quad \quad \text{N} = \text{N} = \text{N} \\ \quad \quad \quad \cdot\cdot \end{array} \quad \text{ionic form - 1}$$

$$\begin{array}{c} +\delta \quad +\delta \quad -2\delta \\ \cdot\cdot \quad \cdot\cdot \quad \cdot\cdot \\ \text{F} - \text{N} \equiv \text{N} - \text{N} \\ \cdot\cdot \quad \cdot\cdot \quad \cdot\cdot \end{array} \quad \begin{array}{l} \text{ionic form - 2} \\ \text{(distributed)} \end{array}$$

b) Transition State Calculations

c) Singlet-Triplet Splitting

66

Table 9. $\text{FN}_3 \rightarrow \text{N}_2 + \text{NF}$ Transition State

Level	Alpha	Beta	NF	NN ₁	NN ₂	Energy
RHF/6-31G*	169.83	79.89	1.3618	1.5890	1.0774	-262.585108
MP2/6-31G*	166.87	71.08	1.3590	1.8165	1.1321	-263.233414
MC6/6-31G*	171.90	99.60	1.3735	1.5711	1.1001	-262.703604

Bond lengths are in angstroms, bond angles are in degrees and energies are in hartrees.

Table 10. $\text{FN}_3 \rightarrow \text{N}_2 + \text{NF}$ TS Vibrational Frequencies

Level	a'					a''	ZPE
RHF/6-31G*	561 i	186	610	1114	2690	295	2448
MP2/6-31G*	410 i	104	427	1077	2113	144	1933
MC6/6-31G*	417 i	180	610	1085	2463	290	2314

Vibrational frequencies and zero point energies (ZPE) are in wavenumbers.

Table 11. $\text{FN}_3 \rightarrow \text{N}_2 + \text{NF}$ Barrier Height

Level	Classical (eV)	Quantum (eV) (includes correction for zero point energy)
RHF/6-31G**/RHF/6-31G*	0.473	0.386
MP2/6-31G**/MP2/6-31G*	1.333	1.205
MC6/6-31G**/MC6/6-31G*	0.565	0.508
MP2/6-31G**/RHF/6-31G*	1.079	0.999
MP3/6-31G**/RHF/6-31G*	0.878	0.790
CCD/6-31G**/RHF/6-31G*	0.790	0.710
ST4CCD/6-31G**/RHF/6-31G*	0.826	0.746

Table 12. FN_3 $3A''$ UHF/6-31G* Energy

	Hartrees	eV (Relative to 'A')
@ 'A' eq	-262.531687	1.927
@ 'A' ts	-262.545538	1.077

These results are shown in Table 13 and Figure 10. As SCF methods will underestimate the singlet energy relative to the triplet, these results should give a lower bound to the actual splitting. Møller-Plesset and coupled cluster calculations were performed at the SCF saddle point geometry to estimate the effect of electron correlation. These results, shown in Table 14, indicate a singlet-triplet splitting of about 1.8–1.9 eV

Our results contradict those reported by Brener, et al. (Reference 103) who examined the singlet-triplet splitting using the MP2 optimized transition state. This state has an extended central N–N bond length, due to the UHF instability mentioned above, and therefore has the crossing on the wrong side of the transition state. The analogous singlet-triplet crossing in HN_3 has recently been determined by Alexander and Dadigian (Reference 104) using MCSCF-CI methods. They find the crossing to occur at a N–N separation of 1.9 Å, which is slightly larger than the 1.68 Å given by our calculation. On inclusion of electron correlation effects, our 1.68 Å separation would increase, due to the larger singlet correlation energy. We may estimate this effect by displacing the curves in Figure 9 to the 1.88 eV gap given by our CCD calculations. When this is done, the singlet-triplet crossing distance is about 1.78 Å, close to the N–N distance predicted by Alexander and Dadigian for HN_3 .

Additional studies of FN_3 are needed at a correlated level of theory to define a standard reaction path leading to $\text{F}[^2\text{P}] + \text{N}_3[^2\Pi]$ reactants. The nature of any barrier in this direction and an analysis of the overall thermodynamics of FN_3 formation should be carried out.

3.2.3 ClN_3 , BrN_3

Our studies to date of FN_3 and $\alpha\text{-N}_2\text{O}_2$ to date have illustrated that *ab initio* calculations at a correlated level of theory are extremely useful in predicting molecular structure, correlating experimental properties and in identifying the spectra of such species. FN_3 is now a well-characterized molecule and is synthesized routinely in several laboratories. This favorable situation, however, does not carry over to the other halogen azides where only limited spectroscopic studies have been performed.

Decomposition studies of halogen azides have been carried out experimentally by several laboratories. Gipstein and Haller (Reference 105) studied the room temperature decomposition of FN_3 and observed N_2F_2 and N_2 as products. Coombe, et al. (Reference 106) examined the 193 and 249 nm photodissociation of ClN_3 , which yields many excited singlet and triplet products. The thermal decomposition of ClN_3 has been studied by Richardson and Setser (Reference 107), who infer that $\text{NCl } [^3\Sigma^-]$ is formed through a crossing of singlet and triplet potential surfaces.

Table 13. FN₃ SCF IRC (Reaction Path)

IRC Point	s	N-N	E('A')	E('A'')
0	0	1.589	-262.585108	-262.545538
2	0.430	1.663	-262.586071	-262.578265
5	0.787	1.724	-262.587979	-262.601709
10	1.442	1.831	-262.592846	-262.635125
20	2.778	2.047	-262.602338	-262.678595

Bond lengths are in angstroms and energies are in hartrees.

Table 14. FN₃ 'A' - 'A'' Higher Order Energies at SCF Geometry

Level	'A' @ RHF ts	'A'' @ RHF ts	Energy Difference (eV) 'A'' - 'A'
SCF/6-31G*	-262.585108	-262.545516	1.077
PUHF		-262.551575	0.912
MP2/6-31G*	-263.221058	-263.148967	1.962
PUMP2		-263.153153	1.848
MP3/6-31G*	-263.218597	-263.149187	1.889
CCD/6-31G*	-263.225497	-263.156454	1.878

Energies are in hartrees.

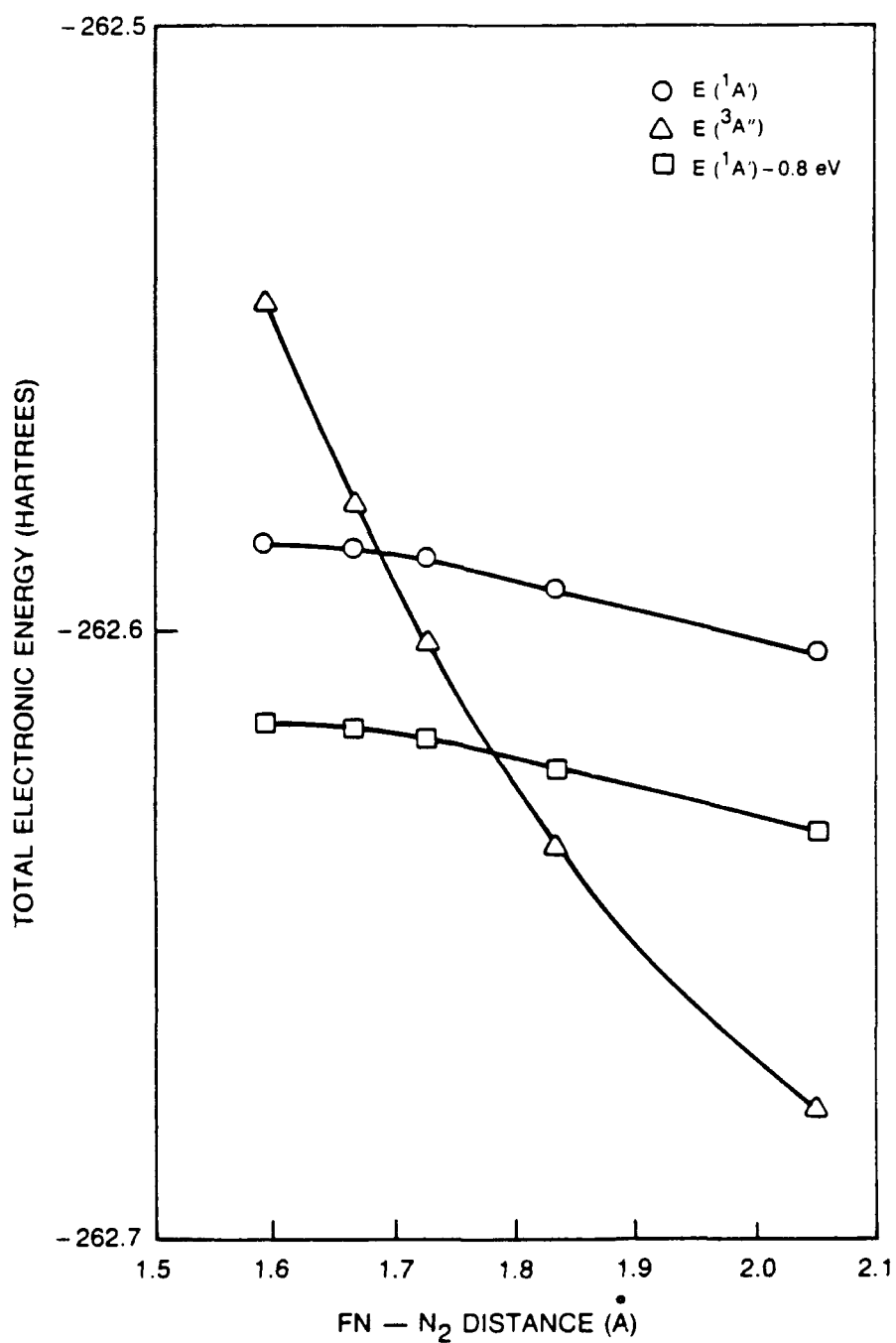


Figure 10. $\text{FN}_3 \rightarrow \text{NF} + \text{N}_2$ Reaction Path

BrN₃ decomposition has been studied by Coombe (Reference 108) who suggests that the N-N bond in BrN₃ is weak, relative to the other hydrogen azides.

Benard and associates (Reference 109) (Rockwell Science Center) have studied the 193 nm photolysis of FN₃ and observed both NF[b¹Σ⁺] and NF[a¹Δ] product states. Their work suggests that either excited FN₃[¹A'] surfaces are involved or that a series of singlet/triplet crossings must occur. More recently, Benard, et al. have carried out a unique thermal dissociation experiment with FN₃ which indicates that, with thermal energy transfer, only the NF[a¹Δ] state is formed. Their adiabatic decomposition mechanism correlates with the location and barrier height predicted by our theoretical studies of this system.

It is clear from the above that the stability and decomposition mechanisms of the halogen azides need to be systematically studied. The key points that need to be addressed theoretically are:

- 1) heat of formation of XN₃ (X = F, Cl, Br)
- 2) zero-point energy analysis
- 3) vibrational (IR) spectra of the ground ¹A' state
- 4) barrier height and width of the transition state leading to NX + N₂
- 5) location of low-lying singlet and triplet reaction surfaces
- 6) analysis of singlet-triplet crossings and branching into NX product channels.

As mentioned above, our current theoretical studies of advanced oxidizer types under this research program have included a preliminary study of the FN₃ molecule. In collaboration with Dr. David Benard's experimental group at Rockwell Science Center, we have made significant progress in characterizing the thermochemistry and stability of FN₃. Our calculated barrier height (~0.6 eV) for decomposition of FN₃ [¹A'] into NF[a¹Δ] + N₂[X ¹Σ_g⁺] and our predicted heat of formation (+565 kJ/mol) have both been confirmed in Benard's studies. On the basis of our past experience, we believe that collaborative efforts are especially fruitful in a systematic characterization of the chemistry of the halogen azide series. Calculations of reaction barrier heights could be used to guide experimental dissociation studies. Experimental frequencies could also be correlated against the prediction of electronic structure calculations.

3.3 Cyclic Boron Structures

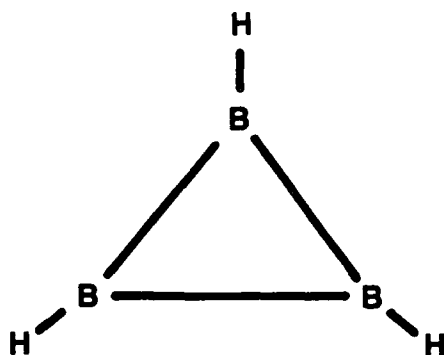
In addition to our studies of Li_mH_n structures, a preliminary analysis of several beryllium and boron compounds was undertaken. There are several beryllium-containing structures that

appear promising. Linear BeH_2 is well characterized both theoretically and experimentally (Reference 110). However, BeH_2 in C_∞ symmetry, which is essentially a $\text{BeH}^+ + \text{H}^-$ ionic complex, has not previously been considered and was a candidate for theoretical study. Nicolaides and Zdzetsis (Reference 23) have examined the corresponding HeH_2 (C_∞) molecule but no stable ground state is indicated other than $\text{He} + \text{H}_2$. The molecular structure, LiBeH_2 (C_{2v}), was also suggested since the Be atom is very electron deficient in BeH_2 and a Lewis adduct may be possible with an alkali. Unfortunately, no stable structure could be found for either of these species, other than the well-characterized $D_{\infty h}$ linear structure of BeH_2 . The performance of $\text{BeH}_2(D_{\infty h})$ as a fuel has previously been analyzed (Reference 111) but its potential is limited by environmental considerations based on the toxicity of BeO .

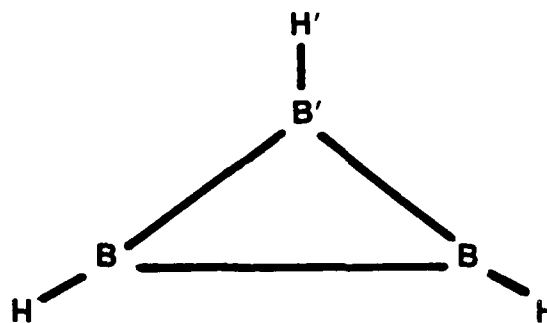
Beyond beryllium, the potential for forming high energy fuels, which offer a significant increase in I_{sp} , diminishes rapidly owing to the molecular weight considerations discussed above and illustrated in Figure 1. However, there are several boron compounds that might be promising candidates, provided they represent local regions of stability and offer a possible route of synthesis. Diborane (B_2H_6) has been extensively studied and evaluated as a rocket fuel. the maximum specific impulse ($P_c = 1000$ psia, expansion to sea level) available with O_2 as an oxidizer is 342 seconds, a value below that offered by H_2/O_2 (389 sec) and $\text{Be}/\text{H}_2/\text{O}_2$ (459 sec). The detrimental effects of molecular weight are apparent with pentaborane (B_5H_9) and decaborane ($\text{B}_{10}\text{H}_{14}$), which yield 319 and 282 seconds, respectively. This led us to suggest that BH_3 adducts may offer higher energy, and hopefully may represent isomeric structures with some measure of stability. Some other possibilities here, which have been examined theoretically by Lammertsma's group, are the $\text{H}_3\text{B} - \text{Li}$ adducts and possibly a $\text{H}_3\text{B} - \text{Be}$ structure, similar to the proposed BeH_2 (C_∞) molecule.

There are several other possibilities if we consider B_2 or B_3 structures. A few compounds which are suggested from similar hydrocarbon structures are shown in Figure 11. Cyclotriborane (B_3H_3) would be the saturated equivalent of cyclopropylene (C_3H_4) in hydrocarbon chemistry. Such a highly strained structure might form substitution compounds which have greater stability but would still be of value as potential fuels. Iminodiborane ($\text{B}_2\text{H}_2\text{NH}$), which is analogous to aziridine (ethylenimine), would have a molecular weight of only 38 and possibly a very high positive heat of formation. Its structure (or stability) was totally unknown. Another possibility is 1,2 epoxydiborane ($\text{B}_2\text{H}_2\text{O}$), the equivalent of ethylene oxide in hydrocarbon chemistry. A somewhat heavier ($\text{MW} = 57$) triboryleneimine or iminotriborane ($\text{B}_3\text{H}_3\text{NH}$), which is similar to azetidine (trimethylenimine) might also be promising. Similar highly strained compounds

Cyclotriborane (B_3H_3)

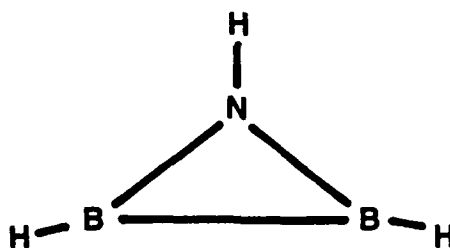


$R_{BB} = 1.734 \text{ \AA}$
 $R_{BH} = 1.178 \text{ \AA}$
 $E = -75.174458$, unstable (2)



$R_{B'H'} = 1.180 \text{ \AA}$ $R_{B'B} = 1.536 \text{ \AA}$
 $R_{BH} = 1.174 \text{ \AA}$ $R_{BB} = 2.032 \text{ \AA}$
 $E = -75.647600$, stable

Iminodiborane (B_2H_2NH)



$R_{BB} = 1.621 \text{ \AA}$ $\angle HBN = 136.2^\circ$
 $R_{BH} = 1.174 \text{ \AA}$ $\angle BNH = 145.3^\circ$
 $R_{NH} = 0.989 \text{ \AA}$ $E = -104.981636$
 $R_{BN} = 1.423 \text{ \AA}$

Frequencies (cm^{-1})

B_1	A_1	A_2	B_2	B_2	B_1	A_1	B_2	A_1	B_2	A_1	A_1
700	818	921	923	989	1000	1110	1268	1423	2878	2916	3965

Figure 11. Cyclic Boron Compounds

containing four or more boron atoms would appear to offer little hope of yielding a specific impulse above 400 seconds.

In a preliminary study of cyclic boron structure, under the present contract, a limited set of calculations were carried out on cyclotriborane (B_3H_3) and iminodiborane (B_2H_2NH) at the SCF level of theory using a 6-31G* basis set. The C_{3v} structure for B_3H_3 is found to be unstable but further studies in C_{2v} symmetry indicate stability. The anion $B_3H_3^-$ is found to be stable as predicted by Lipscomb's rules. Iminodiborane (B_2H_2NH), on the other hand, is a stable structure in C_{2v} symmetry. The optimized geometries and calculated frequencies are shown in Figure 11. Further studies of B_2H_2NH are indicated but our calculated energetics to date indicate that this is not a high-energy structure. We find $\Delta H_f^\circ \approx -20$ kcal/mol for B_2H_2NH , which can be compared with $\Delta H_f^\circ = +12.3$ kcal/mol for diborane. A further negative view is that most iminoboranes eventually form borazine ($B_3N_3H_6$), which is not a high energy fuel. Further studies of other cyclic boron compounds, however, may prove useful.

3.4 Hypervalent Structures

A third category of compounds which may represent energetic molecular conformations are those resulting from orbital hybridization to a high valence state of the central coordinating atom in the molecular species. The existence of such species and the concept of hypervalency have been described many years ago by Pauling (Reference 112). The successful synthesis of hypervalent compounds of second-row elements, such as PF_5 , H_3PO , H_3PF_2 , IF_7 , XeF_6 , has been carried out in several laboratories. The textbook explanation of bonding in such compounds involves contribution from the normally unoccupied d-orbitals on the coordinating atom to form sp^2d (square planar), sp^3d (trigonal bipyramidal), or sp^3d^2 (octahedral) structures. An extension of this argument is that hypervalent molecules formed from first row atoms, such as NF_5 , are not possible since the hybridization energy is too large.

In recent years, quantum mechanical studies have revealed that the bonding in a hypervalent structure such as PF_5 is much more complicated than the simple Pauling hybridization model. In fact, detailed calculations (Reference 113) reveal that PF_5 is stable, even if the d-orbital participation is set to zero. The bonding appears to be better described by sp^2 hybridization to form the trigonal PF_3 ring, with the axial fluorines in a 3-center sp bond. Such a structure can be further stabilized by back-bonding contributions of the normally unoccupied d-orbitals. This new insight into the bonding of hypervalent compounds revives the possibility of forming such structures from first row atoms. Compounds such as NF_5 , NH_3F_2 , OF_4 , ClF_5O and ClF_5

represent hypervalent, high oxidation state structures which represent a new class of possible oxidizers for chemical propulsion systems. For example, Christe (Reference 114) has estimated that theoretical performance calculations for H_2/NF_5 yield a vacuum I_{sp} of 505 sec. We have estimated the optimum performance for a $\text{H}_2/\text{F}_2/\text{NF}_5$ tripropellant ($P_c = 800$ psia, $A/A^* = 20:1$) to be 466 seconds, yielding no significant improvement over the H_2/F_2 system. However, if NF_5 has physical properties as a storable oxidizer, it may be a promising new candidate in comparison with ClF_5 .

The synthesis of such strong oxidizers is an obvious experimental challenge. Christe and collaborators (Reference 115) have succeeded in the synthesis of the adduct, tetrafluoronitronium (V) hexafluoroarsenate (NF_4AsF_6) but all attempts to date to synthesize NF_5 have failed. The structure of NF_4AsF_6 has been confirmed by spectroscopy and magnetic resonance measurements and is known to be ionic, $\text{NF}_4^+\text{AsF}_6^-$. The hybridization of the N atom in NF_4AsF_6 is thus sp^3 , forming the stable tetrahedral NF_4^+ cation, rather than a true pentavalent structure. Further, semi-quantitative arguments by Kutzelnigg (Reference 116) suggest that NF_5 or NH_3F_2 structures will not exist for steric reasons; the charge distribution in the NF_3 planar ring excludes the formation of a short axial N-F bond.

In an effort to more fully understand the competition between steric factors, which might prevent axial bond formation, and the strengths of 3-center bonds, an analysis of NF_5 structures was carried out at both the SCF and MP2 levels of theory using several basis sets. An ionic NF_4^+F^- structure was first examined in light of the stability of Christe's $\text{NF}_4^+\text{AsF}_6^-$ structure. No stable minimum could be located starting the geometry search along the $\text{NF}_4^+ + \text{F}^-$ reaction path. This structure simply decomposes to $\text{NF}_3 + \text{F}_2$. However, two stable covalently bonded structures were found for NF_5 at the SCF level. These structures are illustrated in Figure 12. The D_{3h} (trigonal bipyramid) structure was found to be lower in energy at the SCF/6-31G* level of theory and further, MP2 calculations have indicated that the C_{3v} structure (inverted umbrella) represents a saddle point. The calculated geometry and vibrational frequencies for the D_{3h} structure are given in Tables 15 and 16, respectively, at several levels of theory. These preliminary calculations clearly indicate that careful optimization of the basis set and a correlated level of theory will be required to positively identify the structure and vibrational modes. Introduction of diffuse basis functions and optimization of the d-orbital exponents have a small but important effect on the thermochemistry. Calculations at the MP2 level of theory clearly show a different vibrational pattern owing to the lengthening of the planar NF bond. The most significant

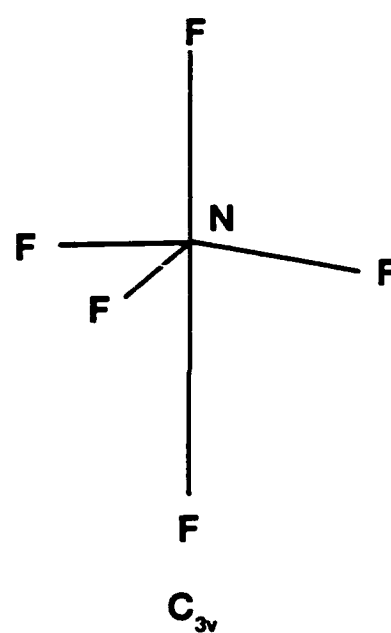
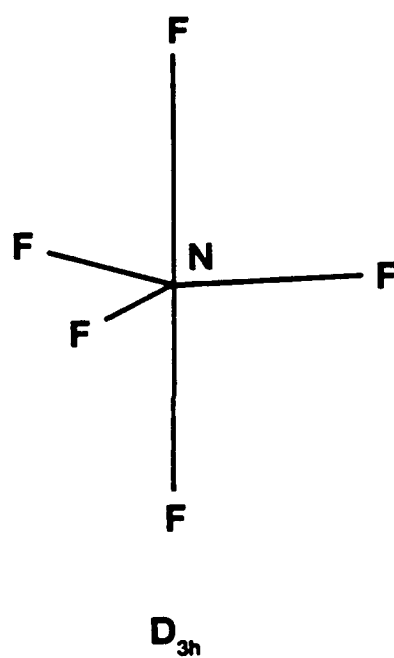


Figure 12. Comparison of D_{3h} and C_{3v} Structures for NF_5

Table 15. *Ab Initio* Structure and Calculated Energy for NF₅ in D_{3h} Symmetry

Theory	d-exponent		r _p	r _h	Energy
	N	F			
SCF/6-31G	-	-	1.3860	1.5926	-550.936601
SCF/6-31G*	0.80	0.80	1.3267	1.5312	-551.103856
SCF/6-31G(d)	0.94	0.76	1.3260	1.5310	-551.104823
SCF/6-31+G*	0.80	0.80	1.3223	1.5473	-551.126800
SCF/6-311G	-	-	1.3765	1.5978	-551.116124
SCF/6-311G*	0.91	1.75	1.3132	1.5457	-551.249831
SCF/6-311G(d)	0.94	0.76	1.3260	1.5310	-551.274677
SCF/6-311G(2d)	1.63	1.32	1.3148	1.5429	-551.292792
	0.54	0.44			
MP2/6-31G*	0.80	0.80	1.4098	1.5472	-552.228780
MP2/6-31G(d)	0.93	1.47	1.3962	1.5538	-552.302405

Energies (hartrees), distances (Å)

r_p = N-F bond length in the plane

r_h = N-F axial bond length

Table 16. Calculated Harmonic Frequencies for NF_5 as a D_{3h} Structure

Theory	Frequencies (cm^{-1})							
	a_2'' axial stretch	e' axial bend	a_1' axial stretch	e' axial bend	e'' asym. bend	a_2'' planar bend	a_1' sym. stretch	e' axial bend
SCF/6-31G	574	235	480	560	568	743	744	1184
SCF/6-31G*	459	276	509	656	663	828	857	1352
SCF/6-31G(d)	452	277	509	656	664	828	858	1351
SCF6-31+G*	155	284	489	649	652	802	855	1353
SCF/6-311G	472	243	442	566	574	718	762	1230
SCF/6-311G*	50	288	481	659	669	829	868	1373
SCF/6-311G(d)	377	278	507	657	666	822	860	1349
SCF/6-311G(2d)	233	286	499	656	664	821	863	1354
MP2/6-31G*	614	173	426	551	578	936	690	969
MP2/6-31G(d)	603	187	394	552	587	922	692	975

observation, however, is that NF_5 is predicted to be vibrationally stable without incorporation of d-orbitals. The classical model of sp^3d bonding is thus clearly incorrect for this system. To check this observation, calculations were carried out on PF_5 at the SCF/6-31G level of theory, both with and without d-orbitals in the basis. Similar stable vibrational structures are found in either case so the energetics of hybridization to sp^3d is not the underlying factor in the stability of these structures.

At the SCF level, the a_2'' stretch is the lowest frequency vibrational mode for NF_5 . Decomposition along this normal mode will probably lead to $\text{NF}_4 + \text{F}$, an endothermic step. However, at the MP2 level, the e' axial bend is predicted to have the lowest frequency. Decomposition along this normal mode would lead to $\text{NF}_3 + \text{F}_2$, clearly an exothermic process. Calculations for PF_5 also indicate that e' is the lowest normal vibrational mode. Detailed calculations of both equilibrium geometries and transition states are clearly required here.

In an attempt to understand the dependence of the a_2'' (s_3) mode of NF_5 on the diffuseness of the basis, several calculations of NF_5 were carried out in C_{3v} symmetry, corresponding to a displacement along the s_3 coordinate. We find a C_{3v} stationary point at the SCF/6-31G* level of theory which is only 0.1 eV higher than the corresponding D_{3h} structure. A harmonic frequency analysis indicates that the C_{3v} structure has all real frequencies with the a' (3) axial stretch mode corresponding to the weakest displacement. This observation suggests that NF_5 , at this level of theory, has a small barrier along this coordinate displacement between the nearly isoenergetic and stationary D_{3h} and C_{3v} structures.

To test the stability of the C_{3v} structure at a higher level of theory, MP2 calculations were carried out with the 6-31G* and 6-311 + G* basis sets. The starting geometry corresponded to the optimized C_{3v} structures found at the SCF level of theory. In both cases, the optimization proceeded uniformly to the lower energy D_{3h} structure. A comparative examination of the SCF charge distributions in the C_{3v} and D_{3h} structures indicates that the C_{3v} structure is very ionic [$\text{NF}_4^+ \text{F}^-$] relative to the more covalently bonded D_{3h} structure. The more diffuse basis sets favor this ionic distribution, resulting in the indicated stability at the SCF level. At the MP2 level of theory, the more ionic C_{3v} structure lies higher in energy and geometry optimization always yields the lower energy, and more covalent, D_{3h} structure.

A final point can be made concerning the possibility of synthesis of this compound. Although a definitive study of the thermodynamics of formation of NF_5 has not yet been

completed, it is clear that the formation of NF_5 is endothermic relative to $\text{NF}_3 + \text{F}_2$, whereas this process is exothermic in the case of PF_5 . It also appears unlikely that NF_5 can be synthesized starting from a salt-type structure $\text{NF}_4^+ \text{R}^-$, since the known tetrahedral compounds have correspondingly lower heats of formation. The key to successful synthesis may lie in the initial preparation of the reactants NF_3 and F_2 . By expanding the bond lengths in NF_3 and F_2 through vibrational excitation, such that the axial and equatorial N-F bonds are more nearly equal, the insertion of F_2 above the NF_3 equatorial plane, followed by a Berry pseudorotation (Reference 117) of an equatorial F atom into an axial position below the plane may occur. This same insertion mechanism is believed to occur in the synthesis of PF_5 . Rapid collisional cooling of the vibrationally hot NF_5 may result in trapping of a stable product.

SECTION 4

CONCLUDING REMARKS

The main goal of this research investigation was to identify and characterize several high energy species that have potential for advanced chemical propulsion systems. Using deliverable specific impulse and storability as the major criteria for the evaluation of new compounds, primary consideration was given to ground state molecular structures, of low molecular weight, which exhibit a high positive heat of formation. We can categorize the compounds that were studied into four (4) groups:

1. light element metal and metal hydride structures as advanced fuels (H_4 , Li_3H , LiH_3 , Li_4)
2. azide-like structures as advanced oxidizers (FN_3 , $\alpha-N_2O_2$, $FNCO$, CO_3 , HN_3 , $FNBF$)
3. cyclic boron/boron hydride structures as advanced fuels (B_3H_3 , B_2H_2NH) and
4. hypervalent compounds as energetic advanced oxidizers (NF_5 and for comparison, PF_5).

A summary of our findings in each of these groups follows:

1. We conclude that the ground states of H_4 (tetrahydrogen), LiH_3 and Li_4 are not promising candidates for storable fuels. None of these molecules exhibit chemical stability in a highly energetic conformation. The system Li_3H , as a planar C_{2v} structure, is stable in its ground state and may offer some promise as a component in a solid hybrid configuration. More work is needed, both theoretically and experimentally on this compound. In particular, the stability against dimer formation, with subsequent formation of LiH and H_2 , needs to be examined.
2. All of the azide-structures are vibrationally stable with high positive heats of formation, excepting $FNCO$. The drawback with these materials is their high molecular weight and high chemical reactivity. However, both FN_3 and $\alpha-N_2O_2$, if encapsulated at about the 10% level as replacement for ammonium perchlorate (AP), yield a significant improvement in the I_{sp} of typical solid formulations. In particular, a 10% replacement of AP with $\alpha-N_2O_2$ yields a 10 second improvement, about the same as that found by the addition of Al metal. Experimental work on $\alpha-N_2O_2$, synthesis and property evaluation, is indicated.

3. The cyclic boron structures B_3H_3 and B_2H_2NH proved to be less energetic than was anticipated. B_2H_2NH is more stable than diborane with a heat of formation ≈ -30 kcal/mol, relative to B_2H_6 . The propensity of such compounds to undergo condensation reactions forming borazines; and their high molecular weight, suggest that these cyclic structures are not prime candidates for consideration as new fuels.
4. The only hypervalent compound studied extensively to date is NF_5 . This molecule has a stability as a trigonal bipyramid structure, with a predicted heat of formation, $\Delta H_f^\circ(0\text{ K}) = +25.1$ kJ/mol. We have outlined a possible synthesis route, starting with NF_3 which has been vibrationally excited via collisional or laser pumping. This system has interesting possibilities as a new liquid oxidizer or in a hybrid formulation with F_2 or O_2 , depending on the physical properties of NF_5 . An experimental program to synthesize NF_5 , starting from NF_3 , is recommended, based on our existing knowledge of the properties of this system.

A final comment is that, based on these studies, we predict advances in oxidizer formulations should be possible, particularly in the area of new solid propellant formulations. We are optimistic that a new oxidizer can be developed through further theoretical and experimental studies which follow this initial investigation. We are not as optimistic concerning the development of a new fuel. *Considering the low molecular weight and relatively weak chemical bond*, it may prove difficult to find a better fuel than H_2 unless progress in free radical stabilization or entrainment of light metals in H_2 is achieved.

SECTION 5

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APPENDIX A

PUBLICATIONS AND PRESENTATIONS

The significant research results obtained under this Contract have been prepared for publication in technical journals or presented at technical meetings. These papers and meetings are listed below. Abstracts of the published papers are included in Appendix B. All of these papers can be found in the open literature. Appendix C contains the latest paper submitted for publication on Li_3H .

A. Technical Reports in Journals and Books

1. "Electronic Structure and Stability of Small Cation and Anion Hydrogen Clusters". J. A. Montgomery, Jr. and H. H. Michels, Proceedings of the 1987 Cooling, Condensation and Storage of Hydrogen Cluster Ions Workshop, Ed. J. T. Bahns, University of Dayton Research Institute, p. 81-94, 1987.
2. "On the Stability of H_4 in C_{3v} Symmetry". J. A. Montgomery Jr. and H. H. Michels, Journal of Chemical Physics, 86, p. 5882-5883, 1987.
3. "On the Structure of the Ground State of H_6^+ ". J. A. Montgomery Jr. and H. H. Michels, Journal of Chemical Physics, 87, p. 771-773, 1987.
4. "Electronic Structure and Stability of Energetic Chemical Species". H. H. Michels and J. A. Montgomery Jr., Proceedings of the High Energy Density Matter (HEDM) Conference, May 12-13, 1987 in Rosslyn, Virginia, p. 219-238, 1987.
5. "The Electronic Structure and Stability of Asymmetric Dinitrogen Dioxide, $\alpha - \text{N}_2\text{O}_2$ ". H. H. Michels and J. A. Montgomery, Jr., Journal of Chemical Physics, 88, p. 7248-7249, 1988.
6. "Theoretical Investigation of Energy Storage in Atomic and Molecular Systems". H. H. Michels and J. A. Montgomery, Jr. Proceedings of the Air Force Second High Energy Density Matter Contractors Conference, 28 Feb. - 2 Mar 1988, Newport Beach California, Editors L. P. Davis and F. J. Wodarczyk, p. 93-100, 1988.
7. "Reply to the Comment on: On the Stability of H_4 in C_{3v} Symmetry". J. A. Montgomery, Jr. and H. H. Michels, Journal of Chemical Physics, 89, p. 3929-3930, 1988.

8. "Theoretical Investigation of Energy Storage in Atomic and Molecular Systems". H. H. Michels, and J. A. Montgomery, Jr., Proceedings of the Air Force Third High Energy Density Matter Contractors Conference, 12-15 March, 1989, New Orleans, Louisiana, Editors T. G. Wiley and R. A. van Opjnen, p. 61-72, 1989.
9. "The Structure and Bonding of Li_3H Ion-Pair States" J. A. Montgomery, Jr., H. H. Michels, O. F. Guner and K. Lammertsma. To be published in Chemical Physics Letters, 1989.
10. "The Electronic Structure and Stability of NF_5 ". H. H. Michels and J. A. Montgomery, Jr. To be submitted to Chemical Physics Letter, 1989.
11. "Theoretical Studies of the Vibrational Spectrum and Thermal Decomposition of Fluorine Azide (FN_3)". J. A. Montgomery, Jr. and H. H. Michels. To be submitted to Chemical Physics Letter, 1989.

B. Presentations

1. "Electronic Structure and Stability of Small Cation and Anion Hydrogen Clusters", H. H. Michels and J. A. Montgomery, Jr., January 1987 Workshop on the Cooling, Condensation and Storage of Hydrogen Cluster Ions, 1-10 January 1987, Menlo Park, California.
2. "Short Wavelength Chemical Lasers Powered by Dissociation of Energetic Molecules", D. J. Benard and H. H. Michels, Special Laser Seminar at AFWL, Kirtland AFB, New Mexico, 27 February, 1987.
3. "Applications in Computational Chemistry: Theoretical Studies of Storable Highly Energetic Molecules", H. H. Michels and J. A. Montgomery, Jr., Leermaker's Symposium, Wesleyan University, Middletown, Connecticut, 8 May, 1987.
4. "Electronic Structure and Stability of Energetic Chemical Species", H. H. Michels and J. A. Montgomery, Jr., High Energy Density Matter Conference, Rosslyn, Virginia 12-13 May, 1987.
5. "The Electronic Structure of H_6^+ ", J. A. Montgomery, Jr. and H. H. Michels, 1987 American Conference on Theoretical Chemistry, Gull Lake, Minnesota, 27-31 July 1987.

6. "Applications in Computational Chemistry: Theoretical Studies of Storable Highly Energetic Molecules", H. H. Michels and J. A. Montgomery, Jr. Invited talk at Louisiana State University, Baton Rouge, Louisiana, 3 September 1987.
7. "Electronic Structure and Energetics of Fluorine Azide (FN_3)", H. H. Michels and J. A. Montgomery, Jr. National American Chemical Society Meeting, New Orleans, Louisiana, 30 August - 4 September 1987.
8. "Theoretical Studies of Hydrogen Cluster Ions", J. A. Montgomery, Jr. and H. H. Michels. Invited Talk at Purdue University, Indiana, 23-24 September 1987.
9. "Theoretical Investigation of Energy Storage in Atomic and Molecular Systems", H. H. Michels and J. A. Montgomery, Jr., AF Second High Energy Density Material Contractors Conference, Newport Beach, California, 29 February - 2 March 1988.
10. "Theoretical Studies of the Vibrational Spectrum and Thermal Decomposition of Fluorine Azide (FN_3)", J. A. Montgomery, Jr. and H. H. Michels. 1988 American Chemical Society National Meeting, Los Angeles, California, 25-30 September 1988.
11. "Theoretical Studies of the Vibrational Spectrum and Thermal Decomposition of Fluorine Azide (FN_3)", H. H. Michels and J. A. Montgomery, Jr. Presented at the AFWL Program Review on the Excited NF Driven Visible Laser, Kirtland AFB, New Mexico, 2 December 1988.
12. "Theoretical Investigation of Energy Storage in Atomic and Molecular Systems", H. H. Michels and J. A. Montgomery, Jr., Third AFAL/AFOSR Contractors Meeting on High Energy Density Matter, New Orleans, Louisiana, 12-15 March 1989.
13. "Electronic Structure and Stability of NF_5 ", H. H. Michels and J. A. Montgomery, Jr., 1989 29th Sanibel Symposia, St. Augustine, Florida, 31 March - 8 April 1989.
14. "Theoretical Studies of Halogen Azides and Azide Like Structures", H. H. Michels and J. A. Montgomery, Jr., Informal Conference on the Chemistry of Energetic Azides, Isocyanates and Related Species, Denver, Colorado, 26-27 April 1989.

15. "*Ab Initio* Determination of Diatomic Dissociation Energies: NF and O₂" J. A. Montgomery, Jr., G. A. Petersson and M. A. Al-Laham. International Conference on Quantum Chemistry in Honor of Professor John A. Pople, Athens, Georgia, 16-19 October 1989.

APPENDIX B-1
ELECTRONIC STRUCTURE AND STABILITY OF SMALL
CATION AND ANION HYDROGEN CLUSTERS

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ABSTRACT

Ab initio calculations of the electronic structure of H_n^- and H_n^+ clusters have been carried out using accurate Gaussian basis sets and with levels of theory up to fourth-order perturbation theory (MP4) and single and double excitation configuration interaction (CISD). The odd hydrogen cation addition sequence, $H_n^+ + H_2 \rightarrow H_{n+2}^+$, appears to be thermodynamically stable for large size cluster formation. The even H_6^+ cation also exhibits surprising stability in D_{2d} symmetry. In contrast, the hydrogen anion addition sequences, $H_n^- + H \rightarrow H_{n+1}^-$ and $H_n^- + H_2 \rightarrow H_{n+2}^-$, appear to be thermoneutral or unstable.

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Published in the Proceedings of the Cooling, Condensation and Storage of Hydrogen Cluster Ion Workshop, Editor - J.T. Bahns, P. 83, 1987.

APPENDIX B-2
ON THE STABILITY OF H_4 IN C_{3v} SYMMETRY

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ABSTRACT

The electronic structure of H_4 in C_{3v} symmetry has been studied by *ab initio* calculations. The ground state energy minimum found in these calculations is shown by vibrational analysis to be a saddle point rather than a stable bound state. The path of steepest descent from the C_{3v} saddle point is found to lead monotonically to dissociation into two H_2 molecules.

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APPENDIX B-3
ON THE STRUCTURE OF THE GROUND STATE OF H_6^+

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ABSTRACT

The electronic structure of H_6^+ has been studied by *ab initio* calculations. It is found that there exist two stable structures, of C_s and D_{2d} symmetries. Post-SCF calculations suggest that the ordering of these states is determined by electron correlation, with the D_{2d} structure lying slightly lower than the C_s structure. It is suggested that the D_{2d} structure is formed in the recent experiments of Kirschner and Bowers.

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APPENDIX B-4

ELECTRONIC STRUCTURE AND STABILITY OF
ENERGETIC CHEMICAL SPECIES

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ABSTRACT

Theoretical quantum mechanical calculations have been carried out for several potentially high energy chemical species. Our research objectives are to identify those light element molecular species that have sufficient internal energy to be useful in advanced chemical propulsion systems. A parametric study of the deliverable specific impulse as a function of available reaction energy and propellant weight indicates that primary consideration should be given to molecular structures that can be formed from hydrogen through boron and that have a molecular weight of 40 or less.

Calculations to date have been performed on three classes of light element compounds: C_{3v} structures such as H_4 and Li_3H , azide structures such as N_3F and $\alpha-N_2O_2$ and cyclic boron structures such as B_3H_3 and B_2H_2NH . We find that the ground state potential energy minimum found for H_4 in C_{3v} symmetry corresponds to a saddle region rather than a stable bound state and that distortion via vibrational or rotational modes leads monotonically to dissociation into two H_2 molecules. In contrast, Li_3H appears to be chemically stable in C_{3v} symmetry. Our studies of asymmetric dinitrogen dioxide ($\alpha-N_2O_2$) indicate a stable azide-like structure in C_s symmetry for the ground $^1A'$ state, with an indicated heat of formation of +430 kJoule/mol. This molecule is a very attractive candidate as an advanced oxidizer. Our preliminary calculations for boron compounds indicate that B_3H_3 is unstable in D_{3h} symmetry but that iminodiborane (B_2H_2NH) is stable in C_{2v} symmetry. The electronic structure, vibrational analysis and thermodynamic stability of these compounds will be described.

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APPENDIX B-5

THE ELECTRONIC STRUCTURE AND STABILITY OF
ASYMMETRIC DINITROGEN DIOXIDE (a-N₂O₂)

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ABSTRACT

The electronic structure of asymmetric dinitrogen dioxide (a-N₂O₂) has been studied by *ab initio* calculations. A stable structure in C_s symmetry, of similar geometry to FN₃, is predicted for the lowest ¹A' state. This structure is characterized by an IR frequency of 1206 cm⁻¹ for the N-O stretch and exhibits a significant activation barrier (65 kJ/mol) for decomposition into N₂ + singlet O₂. This asymmetric form of N₂O₂ has a heat of formation of approximately +500 kJ/mol and is potentially explosive.

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APPENDIX B-6

THEORETICAL INVESTIGATION OF ENERGY STORAGE IN ATOMIC AND MOLECULAR SYSTEMS

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ABSTRACT

Theoretical electronic structure calculations are being carried out for several high energy species that are attractive candidates for advanced chemical propulsion systems. Using deliverable specific impulse and storability as the major criteria for the goodness of new oxidizers or fuels, primary consideration is being given to ground state molecular structures, of low molecular weight, which exhibit a high positive heat of formation. Calculations to date have been carried out on: 1) light element C_{3v} structures H_4 , Li_3H , LiH_3 , Li_4 ; 2) azide-like structures (FN_3 , $\alpha-N_2O_2$, $FNCO$, CO_3 , $FNBF$); 3) cyclic boron structures (B_3H_3 , B_2H_2NH); 4) hypervalent structures (NF_5).

We find that the ground states of H_4 (tetrahydrogen), LiH_3 and Li_4 , as C_{3v} structures, are unstable toward dissociation into diatomic fragments. These molecules do not look promising as storable, high energy chemical species. Li_3H appears to be vibrationally stable as a C_{3v} structure but preliminary studies indicate a low energy content.

All of the azide-like structures are vibrationally stable with high (400–500 kJ/mol) positive heats of formation. The best candidate appears to be asymmetric dinitrogen dioxide, $\alpha-N_2O_2$, which exhibits a heat of formation of +500 kJ/mol and can deliver 450 seconds I_{sp} as a hybrid propellant with hydrogen.

None of the cyclic boron structures examined to date are highly energetic. Their chemistry is further complicated by condensation reactions which cause conversion to higher molecular weight structures.

The hypervalent NF_5 molecule has been studied as a D_{3h} structure, as the ionic $NF_4^+F^-$ form and as a C_{3v} structure. Preliminary calculations indicate stability for NF_5 both as a D_{3h} and C_{3v} structure. Detailed correlated energy calculations are in progress for NF_5 and for several azide structures.

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APPENDIX B-7

REPLY TO THE COMMENT ON: ON THE STABILITY OF H_4 IN C_{3v} SYMMETRY

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ABSTRACT

This is a reply to a response by E. M. Evleth and E. Kassab, On the Stability of H_4 in C_{3v} Symmetry: Comments, JCP, 89, p. 3928, 1988. Their response was to an earlier publication by the above authors (JAM and HHM) entitled: On the Stability of H_4 in C_{3v} Symmetry, JCP, 86, p. 5882, 1987.

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APPENDIX B-8

THEORETICAL INVESTIGATION OF ENERGY STORAGE IN ATOMIC AND MOLECULAR SYSTEMS

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ABSTRACT

Theoretical electronic structure calculations are being carried out for several high energy species that are attractive candidates for advanced chemical propulsion systems. Using deliverable specific impulse and storability as the major criteria for the evaluation of new oxidizers or fuels, primary consideration is being given to ground state molecular structures, of low molecular weight, which exhibit a high positive heat of formation. Calculations to date have been carried out on: 1) light element C_{3v} and C_{2v} structures (H_4 , Li_3H , LiH_3 , Li_4); 2) azide-like structures (FN_3 , $a-N_2O_2$, $FNCO$, CO_3 , HN_3 , $FNBF$); 3) cyclic boron structures (B_3H_3 , B_2H_2NH); and 4) hypervalent structures NF_5 , PF_5).

We have studied the Li_3H system in both C_{3v} (trigonal pyramid) and C_{2v} (planar kite-like) symmetries. Both structures are vibrationally stable, with the C_{2v} symmetry lower in energy at the MP2/6-311G** level of theory. Using either O_2 or F_2 as an oxidizer, Li_3H appears to give about 10% improvement in I_{sp} over LiH .

The energies and pathways for decomposition of FN_3 have been studied. Our calculations, carried out to compliment the experimental studies of FN_3 at Rockwell Science Center, indicate that $NF[a^1\Delta]$ should be efficiently produced by the thermal decomposition of FN_3 . The structure of this molecule, its predicted vibrational spectrum and the role of low-lying triplet states have been examined. A parallel study of the isoelectronic $FNCO$ molecule is in progress.

Further studies of the hypervalent NF_5 molecule indicate vibrational stability only in D_{3h} symmetry. A comparison of the bonding in NF_5 and PF_5 is currently in progress.

A preliminary experiment has shown evidence for formation of $a-N_2O_2$ from the reaction of $O[^1D]$ with N_2O in a neon matrix on a window cooled to $\sim 10K$. A complete vibrational characterization, to positively identify that $a-N_2O_2$ has been formed, is in progress.

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APPENDIX B-9
THE STRUCTURE AND BONDING OF Li_3H
ION-PAIR STATES

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ABSTRACT

Ab initio calculations on Li_3H ion-pair states and a topological analysis of the charge density of the resulting optimized structures are reported. The global Li_3H minimum is a planar C_{2v} structure with $\text{H}^- - \text{Li}_3^+$ ion-pair character. The pyramidal C_{3v} structure, which is 21.5 kcal/mol higher in energy (MP2/6-311 + + G * *), is found to have ionic H-Li bonds, but no Li-Li bonds. Although vibrational analysis indicates this structure to be a true minimum on the potential energy surface, inclusion of the vibrational zero-point energy makes the thermodynamic stability of this structure questionable.

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APPENDIX B-10

THE ELECTRONIC STRUCTURE AND STABILITY OF NF_5

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ABSTRACT

An *ab initio* study of the electronic structure of NF_5 and PF_5 has been carried out using Møller-Plesset perturbation theory. Optimized geometries were calculated at the SCF and MP2 levels of theory using several basis sets, ranging from 6-31G to 6-311 + G*. A vibrational analysis indicates that NF_5 , in D_{3h} symmetry, has all real frequencies, even if d orbital contributions are set to zero. Dissimilar N-F bond lengths ($r_{\text{eq}} = 1.38\text{\AA}$, $r_{\text{ax}} = 1.58\text{\AA}$) are found, in contrast to PF_5 which exhibits nearly equal equatorial and axial bond lengths. A topological analysis of the calculated charge distribution in NF_5 indicates true pentavalent coordination. Our results suggest that synthesis of hypervalent compounds of first row-atoms may be possible.

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APPENDIX B-11

THEORETICAL STUDIES OF THE VIBRATIONAL
SPECTRUM AND THERMAL DECOMPOSITION OF
FLUORINE AZIDE (FN₃)

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ABSTRACT

The vibrational spectrum and decomposition pathways of the highly energetic FN₃ molecule have been studied by *ab initio* methods. Using extended basis sets, harmonic vibrational frequencies and isotope shifts have been calculated from SCF and Møller-Plesset perturbation theory for the ground ¹A' state of FN₃. We find good agreement with the experimental molecular geometry and observed IR frequencies at the MP2/6-31G* level of theory. The transition state for the thermal decomposition of FN₃ into N₂ and NF has been located using both MCSCF and perturbation theory methods. We find a significant dependence of the calculated transition state barrier height on the level of theoretical description. At the MP2/6-31G* level, the optimized RHF wavefunction for the transition state is unstable with respect to a broken-symmetry UHF solution, and therefore multi-reference calculations are required to properly describe the effects of electron correlation. The results are compared with existing experimental spectroscopic data and thermal decomposition studies.

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APPENDIX C

THE STRUCTURE AND BONDING OF Li_3H
ION-PAIR STATES

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ABSTRACT

Ab initio calculations on Li_3H ion-pair states and a topological analysis of the charge density of the resulting optimized structures are reported. The global Li_3H minimum is a planar C_{2v} structure with $\text{H}^- - \text{Li}_3^+$ ion-pair character. The pyramidal C_{3v} structure, which is 21.5 kcal/mol higher in energy (MP2/6-311 + + G * *), is found to have ionic H-Li bonds, but no Li-Li bonds. Although vibrational analysis indicates this structure to be a true minimum on the potential energy surface, inclusion of the vibrational zero-point energy makes the thermodynamic stability of this structure questionable.

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